

FUNDAMENTAL STUDIES OF ION INJECTION AND TRAPPING
OF ELECTROSPRAYED IONS ON A
QUADRUPOLE ION TRAP MASS SPECTROMETER

By

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“The important thing is not to stop questioning. Curiosity has its own reason for existing. One cannot help but be in awe when he contemplates the mysteries of eternity, of life, of the marvelous structure of reality. It is enough if one tries merely to comprehend a little of this mystery everyday. Never lose a holy curiosity.”

– Albert Einstein

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Abstract of Dissertation Presented to the Graduate School
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FUNDAMENTAL STUDIES OF ION INJECTION AND TRAPPING
OF ELECTROSPRAYED IONS ON A
QUADRUPOLE ION TRAP MASS SPECTROMETER

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The quadrupole ion trap is a highly versatile and sensitive analytical mass spectrometer. Because of the advantages offered by the ion trap, there has been intense interest in coupling it to ionization techniques such as electrospray which form ions externally to the ion trap. In this work, experiments and computer simulations were employed to study the injection of electrosprayed ions into the ion trap of a Finnigan MAT LCQ LC/MSⁿ mass spectrometer.

The kinetic energy distribution of the ion beam was characterized and found to be relatively wide, a result of the high pressures from the atmospheric pressure source. One of the most important experimental parameters which affects ion injection efficiency is the RF voltage applied to the ring electrode. A theoretical model was fit to experimental data allowing the optimum RF voltage for trapping a given m/z ion to be predicted.

Computer simulations of ion motion were performed to study the effect of various instrumental parameters on trapping efficiency. A commercially available ion optics

program, SIMION v6.0, was chosen because it allowed the actual ion trap electrode geometry including endcap holes to be simulated. In contrast to previous computer simulations, SIMION provided the ability to start ions outside the ion trap and to simulate more accurately the injection of externally formed ions. The endcap holes were found to allow the RF field to penetrate out of the ion trap and affect ions as they approached the ion trap. From these simulations, a model for the process by which injected ions are trapped was developed.

Using these computer simulations, techniques of improving trapping efficiency were investigated. Most previous techniques perturb ions which are already in the ion trap and therefore cannot be used to accumulate ions; the ability to accumulate ions is a necessity with ionization sources such as electrospray which form ions continuously. One such novel technique for improving trapping efficiency, phase-sympathetic injection, is presented. It was based on the observation that for a given m/z , ions injected at different kinetic energies were trapped at different RF phases. Three-fold increases in trapping efficiency were experimentally observed for m/z 106.1.

CHAPTER 1 INTRODUCTION

The quadrupole ion trap has evolved from an ion storage device used by physicists to one of the most powerful instruments for chemical analysis today. Since its commercialization in 1984 by Finnigan MAT,¹ the ion trap has become a highly sensitive, versatile, and inexpensive mass spectrometer. Many important technological advancements in ion trap operation have come from an ever-increasing understanding of the fundamental operation of the ion trap. These advancements can be divided into three general categories: ion trapping, ion storage and manipulation, and ion detection. This dissertation focuses on ion trapping, specifically the trapping of ions which have been formed externally to the ion trap.

Early commercial ion trap instruments formed ions directly inside the ion trap using either electron ionization or low pressure chemical ionization; however, many modern ionization techniques such as fast atom bombardment, electrospray, and atmospheric pressure chemical ionization cannot be performed inside the ion trap.^{2,3} As a result, the ions must be formed externally and then transported to the ion trap and trapped. Trapping these externally formed ions is not a trivial task because the ions must enter at the correct phase of the RF drive voltage in order to take on stable trajectories. In addition, excess kinetic energy must be removed from these ions to prevent them from eventually escaping from the ion trap.

Overview of Dissertation

This dissertation presents a detailed investigation of trapping ions formed externally by electrospray ionization. A better understanding of the processes by which injected ions are trapped was deemed necessary to insure efficient trapping, especially over a wide range of masses. Some aspects of ion injection which are unique to high pressure ionization sources such as electrospray will be presented. The effects of parameters such as the RF phase as ions enter the ion trap, the RF voltage applied to the ring electrode, the kinetic energy of the injected ion beam, and the pressure of helium buffer gas will be discussed. Experimental data showing the interrelation of these parameters is given as well as extensive computer modeling to give insight into how injected ions are trapped. From this computer modeling, a practical technique was developed for improving the efficiency with which injected ions are trapped.⁴ This technique is unique in that it does not disturb ions which are in the ion trap and therefore can be used to accumulate ions from continuous ionization sources such as electrospray. Previous techniques for improving trapping efficiency⁵⁻⁷ are only useful for trapping short pulses of ions.

This introductory chapter contains a general description of the ion trap and the fundamental basis of its operation. The history of trapping externally formed ions will be discussed along with many of the techniques which have been developed over the years to improve the efficiency with which injected ions are trapped. Finally, the specifics of the Finnigan MAT LCQ ion trap instrument used for these studies will be described,

including differences in geometry and operation from previous commercial ion trap instruments.

History of the Quadrupole Ion Trap

Ion trap is a general term used to describe a device which is capable of trapping and storing ions or other charged particles. Interest in ion traps can be traced back to the Heisenberg Uncertainty Principle of an atomic transition,⁸ which states that precise measurements of the energy of an atomic transition require long observation times. As a storage device the ion trap should permit very accurate measurements.

The quadrupole ion trap mass spectrometer is one such ion trapping device which specifically uses electric fields to store ions and then sort and detect them based upon their mass-to-charge ratio (m/z). It was first disclosed by Paul and Steinwedel in a patent filed in 1953.⁹ This patent also described the quadrupole mass filter, which has arguably become the most common mass spectrometer in existence today. However, the quadrupole ion trap is gaining in popularity because it has proven itself as a highly sensitive, versatile, and inexpensive benchtop mass analyzer. Today's popularity of the quadrupole ion trap is ironic since in Paul's original patent it was simply described as "still another electrode arrangement." The importance of the quadrupole ion trap in both fundamental particle physics and analytical mass spectrometry was recognized with the presentation of the 1989 Nobel Prize in Physics to Wolfgang Paul^{10,11} and Hans Dehmelt¹² for the development of the ion trap technique.

Ion Motion in a Quadrupole Field

The basic design of the ion trap has not changed much in the past 40 years. The ion trap consists of a ring electrode which is placed between two endcap electrodes (Figure 1-1). A potential difference consisting of a DC voltage, U , and an AC voltage of amplitude (zero-to-peak), V , and angular frequency, Ω , is applied between the ring electrode and the two endcap electrodes. The motion of ions in the dynamic electric field created can be calculated from the solutions of a second-order linear differential equation described by the mathematician Mathieu in 1868.¹³ The theory of the quadrupole ion trap that will be described in this chapter has been reviewed extensively.¹⁴⁻¹⁶ This account is by no means complete but is intended to provide the reader with some basic understanding of ion motion in quadrupole ion traps.

The main characteristic of a quadrupole field is the linear dependence of the electric field strength with displacement from the center. In Cartesian coordinates (x, y, z), this electric field $\mathbf{E}$ can be written as

$$\mathbf{E} = E_0 (\lambda x + \sigma y + \gamma z) \quad (1-1)$$

where E_0 is a position-independent component of the electric field and λ , σ , and γ are constants for each of the three directions. Note that there is no coupling between directions in this quadrupole field, which greatly simplifies the math. Because this oscillator system has no external forces, it is subject to the constraints imposed by Laplace's equation

$$\nabla \cdot \mathbf{E} = 0 \quad (1-2)$$

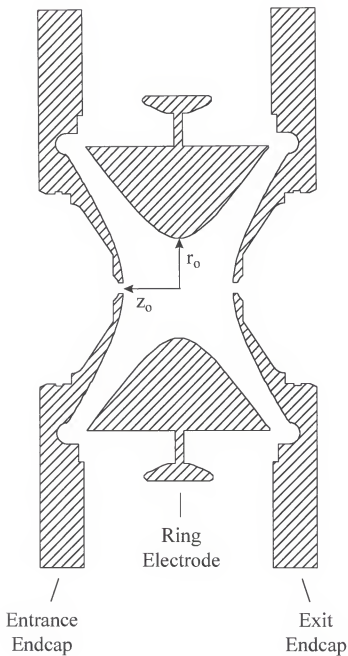


Figure 1-1 – Cross-section of a quadrupole ion trap. The three hyperbolic electrodes (one ring and two endcaps) enclose the trapping volume. Holes in the entrance and exit endcaps allow ions to enter and exit the ion trap. The distances r_0 and z_0 are the radius of the ring electrode and the shortest distance from the center of the ion trap to the endcap electrode, respectively.

Subjecting equation 1-1 to this constraint yields

$$\lambda + \sigma + \gamma = 0 \quad (1-3)$$

Although there are an infinite number of solutions for equation 1-3, the one that is of interest to rotationally symmetric, three-dimensional quadrupole ion traps is

$$\lambda = \sigma \quad \gamma = -2\sigma \quad (1-4)$$

Incidentally, the solution

$$\lambda = -\sigma \quad \gamma = 0 \quad (1-5)$$

is perhaps one of the most trivial, but it describes a device which has no field component in the z-direction. This device is in fact the two-dimensional quadrupole mass filter. Other possible solutions can be imagined which satisfy equation 1-3, but none of them has been explored to any practical ends.

Substituting the relationships in equation 1-4 into equation 1-1, an equation for the electric field inside the quadrupole ion trap is obtained. From this, the potential, Φ , within the device can be calculated by simply integrating.

$$\Phi(x, y, z) = -\frac{1}{2} E_0 \lambda (x^2 + y^2 - 2z^2) \quad (1-6)$$

Because of the rotational symmetry of the ion trap, this equation can also be written in cylindrical polar coordinates (r, ϕ, z). The z coordinate is defined as the center-to-endcap position, or axial position. The r coordinate is defined as $(x^2 + y^2)^{1/2}$ and is the displacement from the z-axis toward the ring electrode, or radial position. Since the ion trap is rotationally symmetric about the z-axis, ϕ can be neglected.

$$\Phi(r, z) = -\frac{1}{2} E_0 \lambda (r^2 - 2z^2) \quad (1-7)$$

This potential is most often written as the general solution

$$\Phi(r, z) = A[r^2 - 2z^2] + B \quad (1-8)$$

where A and B are constants which depend on the boundary conditions of the particular device and the applied potentials; these constants will be solved shortly. But first, the equations for the surfaces of the electrodes must be derived.

The electrode surfaces are rotationally symmetric about the z-axis so all that is needed are equations for the hyperbolic cross-sections of these hyperboloid surfaces in the r-z plane. The general form of an equation for a hyperbola is

$$\frac{r^2}{a^2} - \frac{z^2}{b^2} = +1 \quad (1-9)$$

For the ring electrode, the r-intercept is defined as r_0 , the radius of the ring (r-intercept = r_0). The parameter b which determines the slope of the asymptote will be decided later and for now will be assigned the value α . A similar treatment can be made for the endcap electrodes which have a z-intercept defined as z_0 , the distance from the center of the ion trap to the closest point on the endcaps (z-intercept = $b = z_0$). As with the ring, the slope of the asymptote will be decided later and for now will be assigned the value β . General equations for these hyperbolic electrodes are shown in equations 1-10 and 1-11.

$$\text{Ring Electrode} \quad \frac{r^2}{r_0^2} - \frac{z^2}{\alpha^2} = +1 \quad (1-10)$$

$$\text{Endcap Electrodes} \quad \frac{r^2}{\beta^2} - \frac{z^2}{z_0^2} = -1 \quad (1-11)$$

where α/r_0 and z_0/β are the slopes of the asymptotes for the ring and the endcap electrodes, respectively. One commonly used constraint for the electrodes is to require the asymptotes of the ring and the endcaps to have the same slope.

$$\frac{\alpha}{r_0} = \frac{z_0}{\beta} \quad (1-12)$$

which can then be substituted into equation 1-10.

$$\text{Ring Electrode} \quad \frac{r^2}{r_0^2} - \frac{\beta^2 z^2}{r_0^2 z_0^2} = +1 \quad (1-13)$$

Rearranging equations 1-13 and 1-11

$$\text{Ring Electrode} \quad r^2 = \frac{\beta^2 z^2}{z_0^2} + r_0^2 \quad (1-14)$$

$$\text{Endcap Electrodes} \quad r^2 = \frac{\beta^2 z^2}{z_0^2} - \beta^2 \quad (1-15)$$

and then substituting these equations into the potential equation 1-8 yields the following equations for the potential which must be constant along the surface of the electrodes.

$$\text{Ring Electrode} \quad \Phi(r, z) = A \left[\left(\beta^2 - 2z_0^2 \right) \frac{z^2}{z_0^2} + r_0^2 \right] + B \quad (1-16)$$

$$\text{Endcap Electrodes} \quad \Phi(r, z) = A \left[\left(\beta^2 - 2z_0^2 \right) \frac{z^2}{z_0^2} - \beta^2 \right] + B \quad (1-17)$$

These potentials are constant along the surface of the electrodes when the coefficient of the z^2 term is equal to zero. This occurs when

$$\beta^2 = 2z_0^2 \quad (1-18)$$

Plugging this relationship into equations 1-13 and 1-11 gives the equations for the electrode surfaces.

$$\text{Ring Electrode} \quad \frac{r^2}{r_0^2} - \frac{2z^2}{r_0^2} = +1 \quad (1-19)$$

$$\text{Endcap Electrodes} \quad \frac{r^2}{2z_0^2} - \frac{z^2}{z_0^2} = -1 \quad (1-20)$$

At this point, there is no restriction on either r_0 or z_0 . However, since practical ion traps have truncated electrodes, the contribution of higher-order field distortions has been found to be minimized when¹⁷

$$r_0^2 = 2z_0^2 \quad (1-21)$$

Next, the constants A and B in equation 1-8 can be calculated using boundary conditions established from equations 1-19 and 1-20 for the electrode surfaces. At the equator of the ring electrode, the potential is defined as Φ_0^R .

$$\Phi(r_0, 0) = Ar_0^2 + B = \Phi_0^R \quad (1-22)$$

At the endcap electrode the potential is defined as Φ_0^E .

$$\Phi(0, z_0) = A(-2z_0^2) + B = \Phi_0^E \quad (1-23)$$

The constants A and B can be solved using equations 1-22 and 1-23 to yield the general potential equation for the ion trap

$$\Phi(r, z) = \frac{\Phi_0^R - \Phi_0^E}{r_0^2 + 2z_0^2} \left[r^2 - 2z^2 \right] + \frac{2z_0^2\Phi_0^R + r_0^2\Phi_0^E}{r_0^2 + 2z_0^2} \quad (1-24)$$

The most common mode of operation of the ion trap is to apply the RF and DC trapping voltages to the ring electrode with respect to the endcap electrodes. This simplifies equation 1-24 to yield

$$\Phi(r, z) = \frac{\Phi_0^R}{r_0^2 + 2z_0^2} \left[r^2 - 2z^2 + 2z_0^2 \right] \quad (1-25)$$

With the potential applied to the ring electrode written in terms of U and V, the following potential is obtained:

$$\Phi(r, z) = \left[U - V \cos(\Omega t) \right] \left[\frac{r^2 - 2z^2 + 2z_0^2}{r_0^2 + 2z_0^2} \right] \quad (1-26)$$

From this equation, the potential at any point within the ion trap can be calculated for this particular choice of electrode surface geometries. In order to calculate the motion of ions in this field, the force on the ions is next calculated from this potential using

$$F_r = m \frac{d^2 r}{dt^2} = -e \frac{\partial \Phi}{\partial r} \quad (1-27)$$

$$F_z = m \frac{d^2 z}{dt^2} = -e \frac{\partial \Phi}{\partial z} \quad (1-28)$$

where m is the mass of the ions and e is the charge on the ions. Plugging the potential from equation 1-26 into equations 1-27 and 1-28 and solving for the acceleration yields

$$\frac{d^2 r}{dt^2} = \frac{-2e}{m(r_0^2 + 2z_0^2)} \left[U - V \cos(\Omega t) \right] r \quad (1-29)$$

$$\frac{d^2 z}{dt^2} = \frac{4e}{m(r_0^2 + 2z_0^2)} \left[U - V \cos(\Omega t) \right] z \quad (1-30)$$

These equations can be put in the standard form of the Mathieu equation¹³ which is shown below.

$$\frac{\partial^2 u}{\partial \xi^2} + (a_u - 2q_u \cos 2\xi) u = 0 \quad (1-31)$$

where $\xi = \Omega t / 2$ and u is the ion's position in either the radial ($u=r$) or axial ($u=z$) direction.

The reduced parameters a_u and q_u are defined as

$$a_z = -2a_r = \frac{-16eU}{m\Omega^2(r_0^2 + 2z_0^2)} \quad (1-32)$$

$$q_z = -2q_r = \frac{8eV}{m\Omega^2(r_0^2 + 2z_0^2)} \quad (1-33)$$

These equations describe the motion of ions in a pure quadrupole field. From these equations of the force on an ion, the position and velocity of the ion at the next time step can be calculated using numerical integration. However, not all experimental conditions will produce ion motion which is stable within the ion trap. Here, stability is defined as periodic motion within the ion trap which continues indefinitely and is bounded by the maximum volume of the device. In other words, the ions remain in stable trajectories without striking an electrode surface. The parameters a_u and q_u determine whether an ion will have a stable or unstable trajectory and in fact, since the motion in a pure quadrupole field is not coupled between the r and z direction, it is possible for ions to be stable in one direction but not the other. Practical ion stability occurs only when ions are stable in both the r and z directions simultaneously.

The operating parameters a_u and q_u which result in stable trajectories can be calculated and are most commonly displayed graphically as Mathieu stability diagrams. Although an infinite number of regions of stable solutions to the Mathieu equation exist, only the region shown in Figure 1-2 is of interest to this work. In this figure, different points in a_z / q_z space are shown to correspond to different β_r and β_z values. These β_u

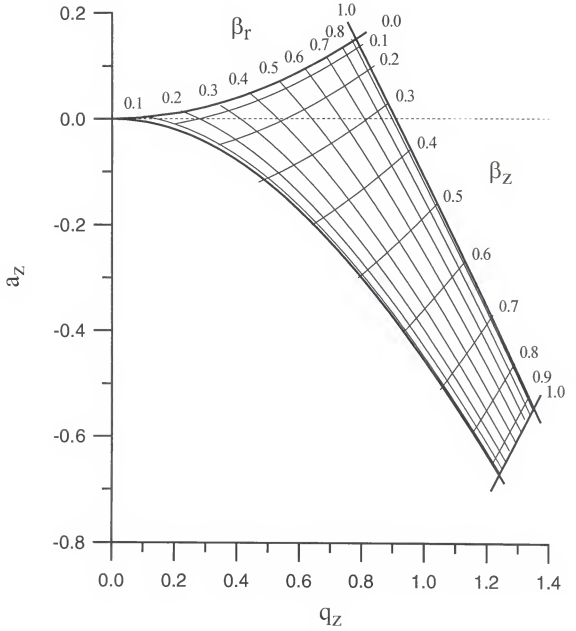


Figure 1-2 – Mathieu stability diagram plotted in a_z and q_z . Ions held at a_z and q_z values inside the $\beta_z=0$, $\beta_z=1$, $\beta_r=0$, and $\beta_r=1$ lines will have stable trajectories. The thinner iso- β lines inside the stability diagram boundaries define the frequency of oscillation of ions within the trap at different operating points in the stability diagram. In this work, the trap was operated with $a_z=0$ (dotted line) so that all ions with a $q_z < 0.908$ were stored.

values determine the fundamental frequency of motion, ω_u , of ions in the r and z directions.

$$\omega_u = \frac{1}{2} \beta_u \Omega \quad (1-34)$$

At this point, a few statements should be made about the stability of ions in the ion trap. First, for a given RF voltage, V, and DC voltage, U, applied to the ring electrode, it is possible to store ions with a range of m/z values simultaneously in the ion trap. Second, for a given RF voltage applied to the ring electrode, ions of decreasing m/z will be stored at increasingly higher q_z , as shown graphically in Figure 1-3. Finally, all of the work presented in this dissertation was performed in an RF-only mode where no DC was applied to the ring with respect to the endcaps ($U=0$ V, $a_z=0$). This causes all m/z ions which have a $q_z > 0.908$ to be unstable within the ion trap.

Ion Detection Techniques

Originally, the ion trap was used as a storage device to allow charged particles to be held and observed for long periods of time. The evolution of the ion trap into a mass spectrometer came later and was driven by advancements in ion detection. In Paul and Fischer's original work, ions were detected by measuring the power absorption from an auxiliary generator applied to the endcap electrodes.^{9,18} The detection circuit was tuned to the frequency of ions at a $\beta_z=0.6$ and a small AC voltage at this frequency was applied across the endcaps. The DC voltage on the ring was then ramped so that ions of increasing m/z consecutively came into resonance with the applied AC voltage. As ions came into resonance, the power absorbed by the ions from the auxiliary generator created a deflection on an oscilloscope. However, even with later improvements to mass-

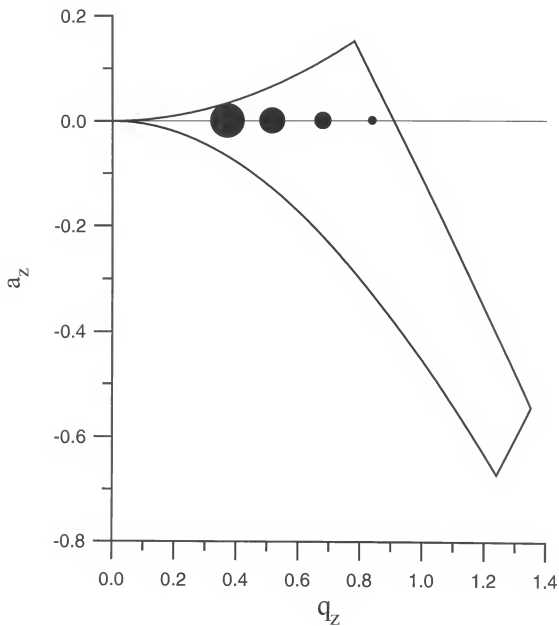


Figure 1-3 – Mathieu stability diagram plotted in a_z and q_z . For a particular RF voltage applied to the ring electrode, the relative q_z values of four m/z ions are shown. Larger circles represent larger m/z ions.

selective detection,¹⁹ a scan speed of 1 Da/s did not allow a practical mass spectrum to be taken over a very large m/z range.

Researchers then turned their attention to mass-selective storage. In this mode, the ion trap was operated with RF and DC voltages applied so that ions of a single m/z were stable inside the trap.⁵ This typically corresponded to the lower corner of the stability diagram. This m/z packet of ions was then ejected from the ion trap through a small hole in one endcap to an electron multiplier detector. Using an electron multiplier provided more sensitive detection and was instrumentally much simpler than the previous tuned circuits. Even though this system produced mass spectra of much higher resolution than mass-selective detection, it offered no clear advantage over quadrupole mass filters.

The ion trap did not become a practical mass spectrometer until the development of mass-selective ejection.²⁰ In this technique known as mass-selective instability, a wide m/z range of ions are stored simultaneously ($a_z=0$). Then, by ramping the RF voltage on the ring electrode, ions of increasing m/z consecutively become unstable in the axial direction as the ions cross the $\beta_z=1$ edge of the stability diagram and are ejected to an electron multiplier. This technique produced a mass spectrum over a wide m/z range and led to the first commercial ion trap mass spectrometer, the Finnigan MAT ITD700, in 1984.¹ Since 1984, a series of technological advancements has improved the sensitivity, resolution, and m/z range of the ion trap. To recount all of these advancements would be beyond the scope of this dissertation; however, some of the more important developments are described below.

Although mass-selective instability scanning required much simpler electronics than previous techniques, the resolution of the spectra was not very high, especially at

m/z values of a few hundred Daltons. Researchers at Finnigan MAT discovered that the addition of a light buffer gas (hydrogen or helium) at a few mtorr dramatically improved sensitivity and resolution.¹ This is in contrast to quadrupole mass filters, whose sensitivity and resolution are degraded at these pressures.

One of the next major developments in ion trap technology further improved resolution and at the same time improved sensitivity. Because the ion trap stores ions in close proximity to one another, ion-ion interactions (or space charge) cause distortions in the trapping field. Even with relatively small numbers of ions in the trap, substantial degradation in the resolution of ions ejected from the $\beta_z=1$ stability boundary results. It was discovered that by applying a supplementary dipolar field of approximately $6 V_{pp}$ to the endcap electrodes 180° out-of-phase, resolution could be substantially improved.²¹ This dipolar field is usually applied at a frequency of ion motion just inside the $\beta_z=1$ stability edge. The improvement in resolution occurs because a uniform electric field is created in the axial direction which reduces ion shielding and therefore space charge effects. As the ions are ramped toward the q_z value corresponding to this applied frequency, their motion comes into resonance with this applied field so the ions gain kinetic energy and are ejected in a tighter packet. The q_z value at which the ions are ejected is defined as q_{ej} . With this technique, known as axial modulation or resonant ejection, good resolution and peak shape can be obtained even with more ions in the ion trap (and therefore larger space charge effects), resulting in better sensitivity. Resonant ejection was later used to extend the m/z range of the ion trap by reducing the q_{ej} value used.²²

One of the most profound developments in ion trap operation came in 1984 but was not disclosed to the public until 1992, when Finnigan MAT announced that all commercial ion trap instruments did not conform to the ideal geometry described by equation 1-21.^{23,24} The first generation of Finnigan MAT ion trap instruments used an $r_0=10$ mm and a $z_0=7.83$ mm (instead of the theoretical $z_0=7.07$ mm). It was discovered that higher-order fields caused by endcap holes, electrode truncation, and imperfect machining and assembly were causing m/z assignments to be compound-dependent. Increasing the z_0 displacement created strong higher-order fields within the ion trap but actually improved the quadrupole nature of the field near the center where most ions reside. In addition, it was discovered that stretching the ion trap axially also improved resolution.²⁵

Injection and Trapping of Externally Formed Ions

Before 1994, all commercial ion trap systems formed ions directly inside the ion trap using either electron ionization or low pressure chemical ionization. This ionization method made the ion trap system very compact and eliminated the ion optics which need to be tuned for efficient ion transmission into the ion trap. One example where forming ions inside the ion trap is impossible is electron-capture negative chemical ionization. Here, negative ions are formed by capture of thermalized electrons.²⁶ This normally requires high pressures to slow the electrons down to thermal energies. Even if it were possible to use high enough pressures within the ion trap, it is still impossible to generate cold electrons because the RF field imparts high kinetic energies on the free electrons.^{27,28} In addition, many other modern ionization techniques such as fast atom bombardment,

electrospray, atmospheric pressure chemical ionization, inductively coupled plasma, and glow discharge cannot be performed inside the ion trap because of the inherent nature of these ionization techniques. As a result, the ions must be formed externally and then transported to the ion trap and trapped.

There are several other reasons why it is more practical to form ions externally. First, because of the relatively long storage time of ions in the ion trap (>10 ms), ion-molecule reactions are observed between ions in the ion trap and any neutral molecules which are present.^{29,30} By introducing the neutral molecules into an external ionization source, the partial pressure of neutrals in the ion trap can be minimized, dramatically reducing the number of ion-molecule reactions. Not only are ion-molecule reactions a problem, but so are ion-ion interactions, specifically ion-ion recombination. When electrons are introduced into the ion trap volume, both positive and negative ions may be formed from the neutrals that are present. These positive and negative ions can then recombine and reduce the sensitivity of the instrument.³¹ By forming the ions externally, ions of a single polarity can be transported to the ion trap.

Problems Associated with Ion Injection

There are several problems associated with the transport of ions to the ion trap and the subsequent efficient capture of these ions. First, high pressure ionization sources such as electrospray require specialized ion optics to efficiently transport ions to the ion trap; some of these issues will be addressed in Chapter 2. The second and perhaps most challenging aspect of ion injection is the efficient trapping of ions. The idea of trapping externally formed ions appeared in a 1959 paper.¹⁸ In this paper, E. Fischer said "... es

ist unmöglich, ein Ion von außen in das Feld einlaufen zu lassen, - was auch ohne Rechnung verständlich ist, - das Ion darf erst im Raum zwischen den Elektroden aus einem neutralen Molekül gebildet werden” [p. 5] (... it is impossible to introduce an ion from outside the field, - which can be understood even without calculations-, the ion must be produced in the space between the electrodes from a neutral molecule). It seems that the inventors of the ion trap had this idea in mind from the very beginning. Paul *et al.* used the German word “Käfig” meaning “cage” rather than “Falle” which means “trap”. They felt the device was a confinement device, not a trapping device. Fortunately, the ion trap is capable of trapping externally formed ions because Fischer was only partially correct.

Fischer was correct that with a constant RF voltage applied to the ring electrode, injected ions cannot be trapped indefinitely because of the excess kinetic energy which allowed them to enter the ion trap in the first place. This can be visualized using a simple pseudopotential well model of the trapping field inside the ion trap.³² An ion which is formed within the ion trap will oscillate within a pseudopotential well (Figure 1-4a). However, an ion which is injected from outside the ion trap will have sufficient kinetic energy to roll up the pseudopotential well and escape (Figure 1-4b). One way to prevent this is to damp this excess kinetic energy before the ion can escape.

Methods of Improving Trapping Efficiency

In order for the ion trap to indefinitely trap ions, some method of removing excess kinetic energy from the injected ions is necessary. Collisional damping with a buffer gas is the most common method and although it works, it is rather inefficient because of the

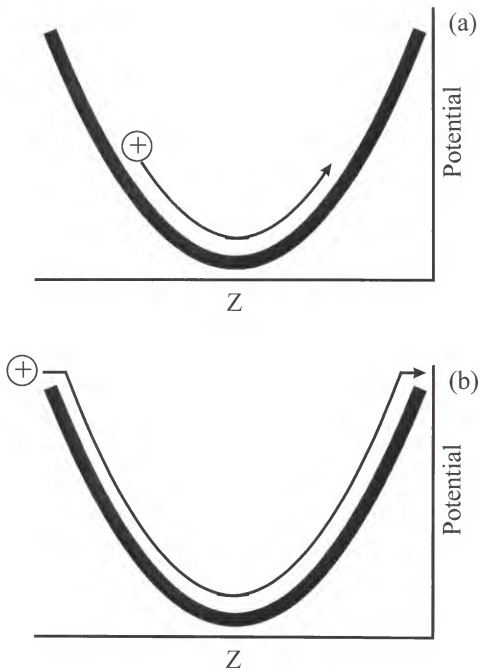


Figure 1-4 – Pseudopotential well representation of the ion trap for an ion (a) formed within the ion trap and (b) injected from outside. Note that the injected ion has sufficient kinetic energy to escape the trapping field. Adapted from reference 3.

low pressures of damping gases which are typically used.²⁹ As a result, other techniques for trapping injected ions have developed, including dynamic trapping, which was disclosed in a patent⁵ and several theoretical papers³³⁻³⁷. In this technique, a pulse of ions is introduced into the ion trap with the RF voltage off, once the ions reach the center of the ion trap, the RF voltage is abruptly turned on. Instead of the ions being formed inside the trapping field, the trapping field is formed around the ions. Although a high trapping efficiency is theoretically predicted, it is experimentally challenging to obtain short rise times with the RF voltage and to accurately synchronize the RF voltage turn on with the ions reaching the center of the ion trap.

Dynamic trapping was demonstrated experimentally for ions laser desorbed from the ring electrode.³⁸ The relatively slow rise time of the RF voltage ($\approx 175 \mu\text{s}$) allowed the ions to reach the center of the ion trap before experiencing a strong trapping field. A similar technique, demonstrated by Doroshenko and Cotter, used a modified RF control circuit to reduce the RF rise time from $175 \mu\text{s}$ to about $25 \mu\text{s}$.³⁹ In both cases, the relatively slow rise time compared to the RF period eliminated the need for complicated phase synchronization which computer simulations had predicted to be important.^{33,34} More recently, Qin and Chait described matched dynamic trapping which is similar to dynamic trapping except after the RF is ramped up, the RF is ramped back down to a predetermined storage level.⁴⁰ Experimentally measured trapping efficiencies of 39% were obtained for matched dynamic trapping compared to 10% with conventional dynamic trapping for the $[\text{M}+\text{H}]^+$ ion of bombesin at m/z 1619.8.

Another technique which has been used to remove kinetic energy from injected ions employs a dipolar DC pulse across the endcaps to decelerate short pulses of injected

ions.^{5,6,41} A similar technique took advantage of the fact that ions oscillate in the ion trap at a particular frequency ω_z . Moore and Gulick demonstrated that kinetic energy could be removed from the axial oscillation of ions by applying an alternating damping voltage across the endcap electrodes.⁷ This quadrupolar damping voltage was applied at a frequency near, but not equal to the frequency of the ions. Using a frequency near resonance causes a small quantity of axial kinetic energy to be removed, postponing the ion from hitting an electrode and allowing more time for collisional damping to take place. Using a frequency at resonance will often cause the ions to quickly leave the ion trap before the ions can be collisionally cooled. Since the phase of the damping voltage is very important, the damping voltage was run at a frequency which is a submultiple of the main RF frequency. In this case, the damping voltage was chosen to be one-fifth of the RF frequency or 54 kHz. Using this method, it was found experimentally that about 50% of injected ions could be trapped.⁷ Using numerical simulations of the ion motion, Moore and Gulick also noted that it is not necessary to remove all of the kinetic energy that the ions enter the ion trap with.⁷ For example, they found that removing by collisions only 1 eV from an ion which entered the ion trap with 30 eV was sufficient to allow the ion to be trapped indefinitely, provided the ion entered the ion trap at an appropriate RF phase.

All of these techniques have shown the potential for very high trapping efficiencies (>50%); however, they are all designed for pulsed ionization techniques which generate short pulses of ions (<30 μ s). These techniques cannot be used to accumulate multiple packets of ions because they disturb ions which are already in the ion trap. For example, in order to trap a second packet of ions with dynamic trapping, the trapping field must be turned off to allow the second packet to enter. This will cause the

first packet of trapped ions to be lost. An even more challenging case than trapping multiple packets of ions is to efficiently trap a continuous beam of ions. Ionization techniques such as electrospray form ions continuously and often in such low abundance that ions must be accumulated in the ion trap (for >100 ms) in order to obtain adequate signal-to-noise ratios.⁴² The only technique which can be used with continuous ionization sources is collisional damping; however, it has been estimated that less than 5% of the total ions are trapped.^{40,43} To develop a more efficient technique for use with continuous ionization sources, a better understanding of the processes by which injected ions are trapped was needed. Chapters 2 and 3 of this dissertation will present a detailed description of the experimental parameters that affect the trapping of injected ions. A model of the processes involved in ion trapping is proposed. In Chapter 4, three methods of improving trapping efficiency from continuous sources will be presented. These include a novel technique called phase-sympathetic injection⁴ which has demonstrated three-fold improvements in trapping efficiency.

The Finnigan MAT LCQ LC/MSⁿ Quadrupole Ion Trap Mass Spectrometer

A modified Finnigan MAT LCQ LC/MSⁿ quadrupole ion trap mass spectrometer^{44,45} was used for all studies. A schematic of the instrument is shown in Figure 1-5 and will be described in more detail in Chapter 2. Briefly, ions are formed by electrospray ionization⁴⁶⁻⁴⁹ at atmospheric pressure and collected by a heated metal capillary. Ions exiting the heated capillary are focused by a tube lens and then pass through a skimmer cone into a 2 in long RF-only octopole ion guide. After a lens, which serves as a conductance limit, a second octopole transports ions into the ion trap. For all

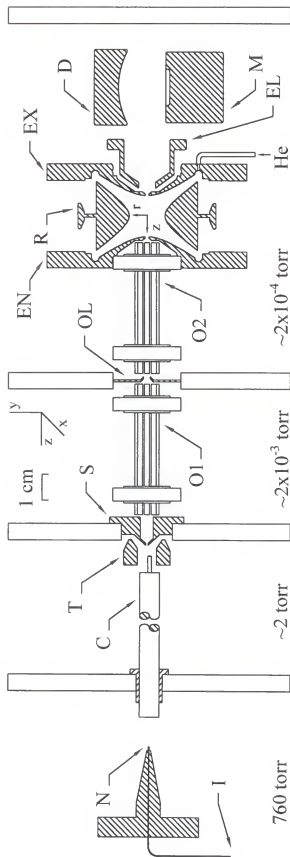


Figure 1-5 – Schematic of Finnigan MAT LCQ LC/MSⁿ quadrupole ion trap mass spectrometer equipped with electrospray ionization source. I=sample inlet; N=electrospray needle; C=heated capillary; T=tube lens; S=skimmer cone; O1=first octapole ion guide; OL=inter-octapole lens; O2=second octapole ion guide; EN=entrance endcap; R=ring electrode; EX=exit endcap; EL=exit endcap; D=electron dynode; M=electron multiplier. The approximate pressure in each region of the system is shown as well as the gas inlet (He) which supplies the helium buffer gas directly into the ion trap. Because of the pumping conductance out of the ion trap, the helium pressure in the ion trap is approximately 10 to 20 times higher than that in the chamber.

of these experiments, a helium buffer gas pressure of approximately 1.5 mtorr in the ion trap was used. Note that in contrast to previous Finnigan MAT ion traps, the LCQ has only a single hole in each endcap electrode to allow ions to enter and exit.

As with previous Finnigan MAT ion trap instruments, the LCQ does not use the ideal electrode spacing $r_0^2=2z_0^2$ given in equation 1-21. The LCQ used in these studies had $r_0=7.07$ mm and $z_0=7.85$ mm, instead of the theoretical $z_0=5$ mm (previous Finnigan MAT ion traps had $r_0=10.0$ mm and $z_0=7.83$ mm).⁴⁴ The drive frequency, $\Omega/2\pi$, used on the LCQ is 760 kHz (previous Finnigan MAT ions traps used $\Omega/2\pi\approx 1.1$ MHz); this lower frequency combined with the smaller r_0 give it an increased m/z range. The m/z range of the instrument can be calculated from a rearranged version of equation 1-33.⁵⁰

$$\left(\frac{m}{z}\right)_{\max} = \frac{8eV_{\max}}{q_{ej}\Omega^2(r_0^2 + 2z_0^2)} \quad (1-35)$$

where $V_{\max}$ is the maximum RF voltage and q_{ej} is the q_z value ions are ejected from the ion trap using resonant ejection. Two different values of q_{ej} were used in these studies, creating two different maximum m/z ranges for the instrument. These and several other LCQ instrumental parameters are summarized in Table 1-1.

Table 1-1 – LCQ ion trap operating parameters

Parameter	Value	Unit
r_0	7.07	mm
z_0	7.85	mm
$\Omega/2\pi$	760	kHz
Max RF Voltage	8500	V_p
Scan Rate	5555.6	Da/s
Helium Pressure	1.5	mtorr
q_{ej}	0.9 or 0.83	
m/z Range	1850 or 2000	Da

A block diagram of the major electronics systems which control the RF voltages applied to the ring electrode and the octopoles, and the waveforms applied to the endcap electrodes is shown in Figure 1-6. Custom instrument control software was used to control all of these instrumental parameters and to allow custom experiments and scans to be performed.⁵¹

Using the parameters listed in Table 1-1, several of the equations presented in this chapter can be simplified. Below are several relationships which can be used to calculate many of the values used in this dissertation.

$$q_z = 0.195 \frac{V}{m/z} \quad (1-36)$$

Since it is impractical to directly measure the RF voltage on the ring electrode, a new parameter was defined, low mass cut off or LMCO. The LMCO is defined as the m/z which has a $q_z = q_{ej}$ for a given RF voltage applied to the ring electrode; all higher m/z ions will have a $q_z < q_{ej}$.

$$LMCO = \frac{8eV}{q_{ej}\Omega^2(r_o^2 + 2z_o^2)} \quad (1-37)$$

$$LMCO = 0.195 \frac{V}{q_{ej}} \quad (1-38)$$

where LMCO is expressed in Da and V is expressed in V_p.

$$LMCO = \frac{q_z}{q_{ej}}(m/z) \quad (1-39)$$

These equations are used throughout this dissertation to interconvert between these commonly used variables.

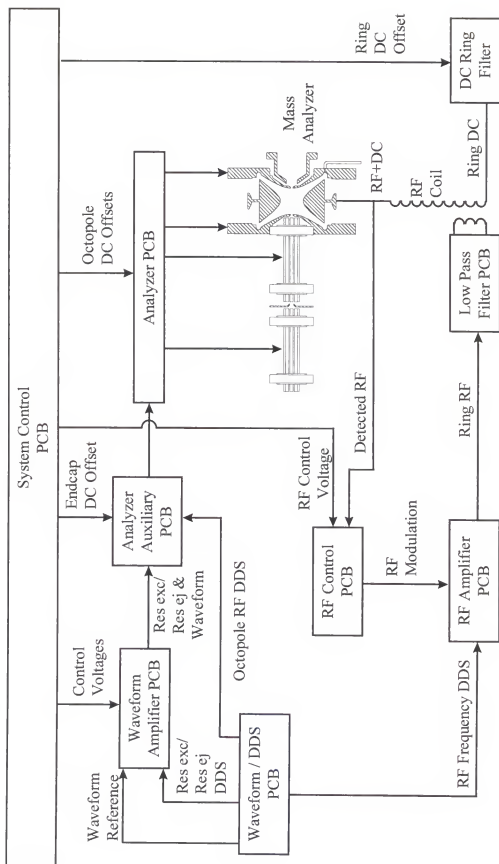


Figure 1-6 – Block diagram of LCQ RF and waveform electronics. Adapted from reference 52.

CHAPTER 2

ION TRANSPORT AND TRAPPING FROM AN ATMOSPHERIC PRESSURE IONIZATION SOURCE

Introduction

This chapter addresses ion injection of electrosprayed ions from a practical, experimental standpoint. Ionization sources which produce ions at atmospheric pressure require a series of differentially pumped vacuum regions in order to generate an acceptably low pressure in the region of the ion trap.² Ions must be transported efficiently through regions of high pressure and this is often done with specialized ion optics. These high pressures and the significant number of collisions which result affect the kinetic energy of the ion beam and can produce a kinetic energy distribution which is relatively wide. Measurements of this kinetic energy distribution will be shown from experimental stopping potential measurements and a theoretical model will be presented.

Next, the effect of the q_z at which the ions are injected will be studied. Different m/z ions are trapped efficiently at different q_z values; a relationship between the optimum q_z and the m/z will be derived. This relationship is found to match well with a theoretically predicted relationship derived from the kinetic energy data. Finally, the issue of trapping a wide range of m/z ions simultaneously will be approached from a practical standpoint. For a given RF voltage applied to the ring electrode, only a narrow range of m/z ions can be trapped simultaneously. By varying the RF voltage during

injection, a wider range of m/z ions may be trapped. A novel algorithm was developed which predicts how to vary the RF voltage during ion injection to trap m/z ions across the desired scan range.

Electrospray: An Atmospheric Pressure Ionization Technique

Electrospray ionization forms charged droplets at atmospheric pressure through the application of high voltage to a needle through which a liquid sample is pumped.⁴⁶⁻⁴⁹ In the Finnigan MAT LCQ instrument (see Figure 1-5), the solution to be analyzed is pumped by a syringe pump through a 100 μm i.d. piece of fused silica (200 μm o.d.) which is placed inside a stainless steel needle (26 ga, 460 μm o.d., 260 μm i.d.) to which approximately +4 kV (for positive ions) is applied. Charged droplets are formed at the tip of the needle and subsequently accelerated toward a 0.37 mm orifice in the vacuum chamber. A concentric flow of nitrogen is passed through the needle around the fused silica to aid in breaking up the droplets at the tip. From there, the analyte is swept into the vacuum system through a heated, stainless steel capillary tube (370 μm i.d., 11.4 cm long). The charged droplets are desolvated by heat ($\approx 200^\circ\text{C}$) as well as by collisions; the resulting species expand in a supersonic jet into the vacuum chamber. Although ions were formed at atmospheric pressure, this first vacuum region (pumped by a 500 L/min mechanical pump) has an average pressure of approximately 2 torr. A positive voltage is applied to the tube lens to focus positive ions through the skimmer cone for transport to an octopole ion guide. The small orifice in the skimmer cone allows the pressure in the first octopole (pumped at 130 L/s by the first stage of the turbomolecular pump) to be approximately 2 mtorr. Finally, the inter-octopole lens serves as the final conductance

limit (0.100 in hole) before a vacuum region (pumped at 260 L/s by the second stage of the same turbomolecular pump) which has a background pressure (without helium buffer gas) of approximately 2×10^{-6} torr. Helium is introduced directly into the ion trap at a pressure of approximately 1.5 mtorr. This flow increases the pressure in the vacuum chamber to approximately 2×10^{-4} torr. Another octopole ion guide transports ions to the ion trap where they can enter the trapping volume through a single hole (0.060 in) in the entrance endcap.

Ions Studied

Thirty different m/z ions were used throughout this dissertation (see Table 2-1). These ions were produced from the electrospray ionization of five different sample solutions. The first sample contained a mixture of lysine, caffeine, met-arg-phe-ala, and Ultramark 1621. The second sample contained a polymeric distribution of polyethylene glycol. The other three samples were individual solutions of serine, bradykinin, and renin substrate. All of the samples were prepared from standards and infused at 3 $\mu\text{L}/\text{min}$ with a syringe pump.

Kinetic Energy Measurements

Since the kinetic energy of ions entering the ion trap is known to affect the trapping of injected ions,⁵³ measurements of the kinetic energy of the ion beam were performed.^{54,55} One of the simplest methods of measuring kinetic energy is by placing a retarding potential on the detector or on an aperture in front of the detector.^{56,57} By increasing the potential applied, the detected intensity for positive ions drops off. The detector signal is the integrated current of ions whose kinetic energy exceeds the potential

Table 2-1 – List of ions studied including the solvent used where ACN = acetonitrile, MeOH = methanol, H₂O = water, and AA = acetic acid (percentage by volume).

m/z	z	Compound	Ion Type	Solvent
106.1	1	serine	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
147.2	1	lysine	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
195.1	1	caffeine	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
262.6	2	met-arg-phe-ala	[M+2H] ²⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
327.2	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
371.2	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
415.3	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
459.3	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
503.3	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
524.3	1	met-arg-phe-ala	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
530.8	2	bradykinin	[M+2H] ²⁺	50:50 MeOH:H ₂ O 2% AA
587.3	3	renin substrate	[M+3H] ³⁺	50:50 MeOH:H ₂ O 2% AA
608.4	1	polyethylene glycol	[M+NH ₄] ⁺	50:50 MeOH:H ₂ O 2% AA
652.4	1	polyethylene glycol	[M+NH ₄] ⁺	50:50 MeOH:H ₂ O 2% AA
696.4	1	polyethylene glycol	[M+NH ₄] ⁺	50:50 MeOH:H ₂ O 2% AA
740.4	1	polyethylene glycol	[M+NH ₄] ⁺	50:50 MeOH:H ₂ O 2% AA
811.5	1	polyethylene glycol	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
880.5	2	renin substrate	[M+2H] ²⁺	50:50 MeOH:H ₂ O 2% AA
1022.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1060.6	1	bradykinin	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
1122.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1222.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1322.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1422.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1522.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1622.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1722.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1759.9	1	renin substrate	[M+H] ⁺	50:50 MeOH:H ₂ O 2% AA
1822.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA
1922.0	1	Ultramark 1621	[M+H] ⁺	50:25:25 ACN:MeOH:H ₂ O 2% AA

on the detector or aperture. A plot of the detected signal versus the applied potential gives the integral of the energy distribution; this type of plot is called a stopping potential curve. In this study, stopping potentials were measured by varying the offset voltage on the second octopole and measuring the resulting number of ions trapped in the ion trap

and then subsequently detected. This measurement was performed for a series of different m/z ions. Also, two different skimmer cone designs were tested to determine the effect of the skimmer on the ion beam kinetic energy. The skimmer cone shown in Figure 2-1a was used in a prototype LCQ instrument whereas the design in Figure 2-1b is the skimmer cone used in the commercial LCQ instrument. The two skimmer cones are identical on the entrance side; however, the exit side of the prototype skimmer is more open than the commercial skimmer, which resembles a narrow tube lens on the exit side. The commercial skimmer design was chosen to minimize the fringe field effect on ions as they enter the first octopole. The narrower opening in this skimmer reduced the effect of the octopole RF voltage on the approaching ions.

Prototype Skimmer Stopping Potentials

Beginning with the prototype skimmer design, stopping potentials using the second octopole offset were performed. From these measurements, the kinetic energy of the ions entering the ion trap can be calculated. The DC offset on the second octopole, V_{O2} , was varied between -10 V and +4 V in 0.25 V increments; the resulting ion signals for five different m/z ions was recorded. These stopping potentials are shown in Figure 2-2 for eight different DC offsets on the first octopole, V_{O1} . The offset on the ion trap, V_{TrapDC} , was held at -10 V. To calculate the kinetic energy distribution from these stopping potentials, the first derivative was taken (Figure 2-3). The average stopping potential, V_{O2Stop} , is defined as the inflection point in the original stopping potential data or the maximum value of the first derivative. From the stopping potentials, the average kinetic energy of the ion beam entering the second octopole can be calculated as $E_{O2}=z[V_{O2Stop}-V_{O2}]$. Or more interestingly, the kinetic energy of the ion beam as it enters

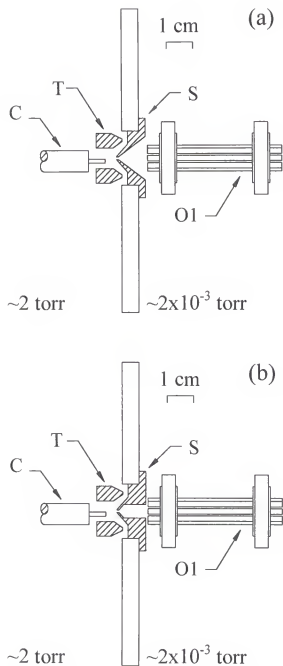


Figure 2-1 – Schematic diagram of two different skimmer cone designs. (a) prototype instrument skimmer cone and (b) commercial instrument skimmer cone. Portion of LCQ ion optics shown with C=heated capillary, T=tube lens, S=skimmer cone, O1=first octopole.

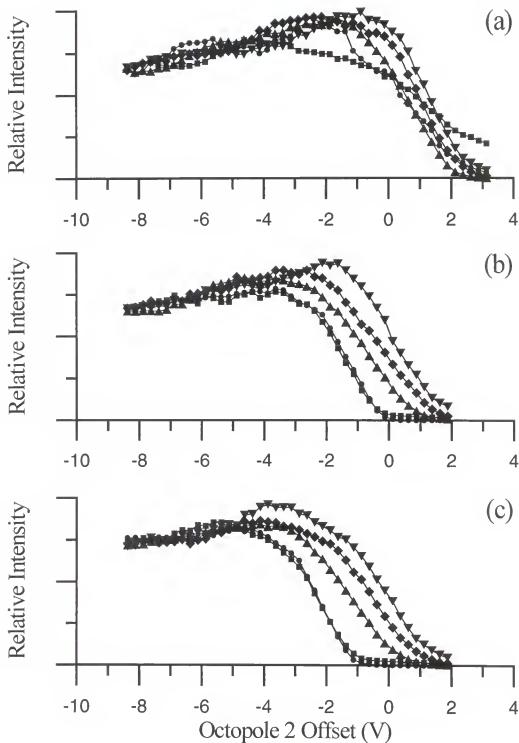


Figure 2-2 – Stopping potentials generated using the second octopole offset, V_{O2} . Signal intensity was normalized to a $V_{O2} = -6$ V. Data are shown for m/z 195.1 (●), m/z 524.3 (■), m/z 1222 (▲), m/z 1522 (◆), and m/z 1822 (▼). Shown for first octopole offsets, V_{O1} , of (a) +1 V, (b) -1 V, (c) -2 V, (d) -3 V, (e) -4 V, (f) -5 V, (g) -10 V, and (h) -20 V.

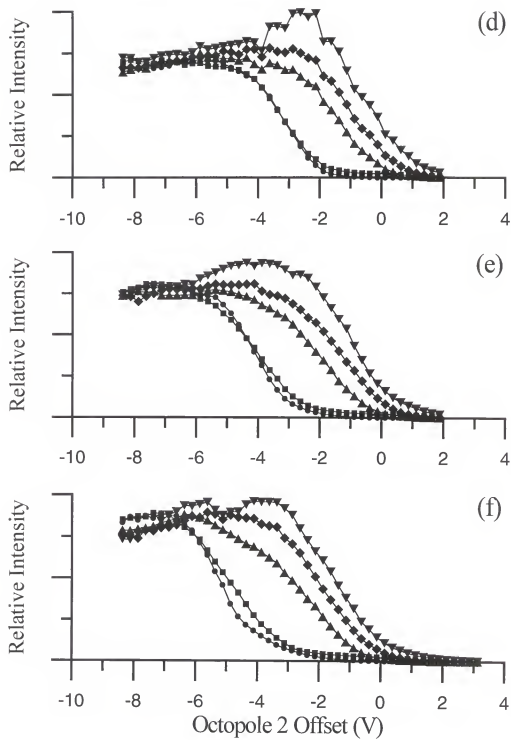


Figure 2-2 – continued.

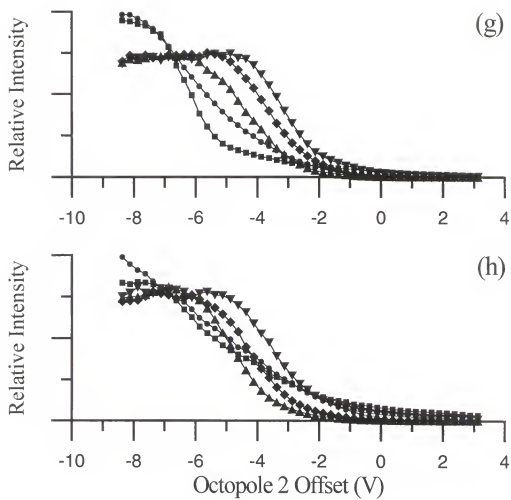


Figure 2-2 – continued.

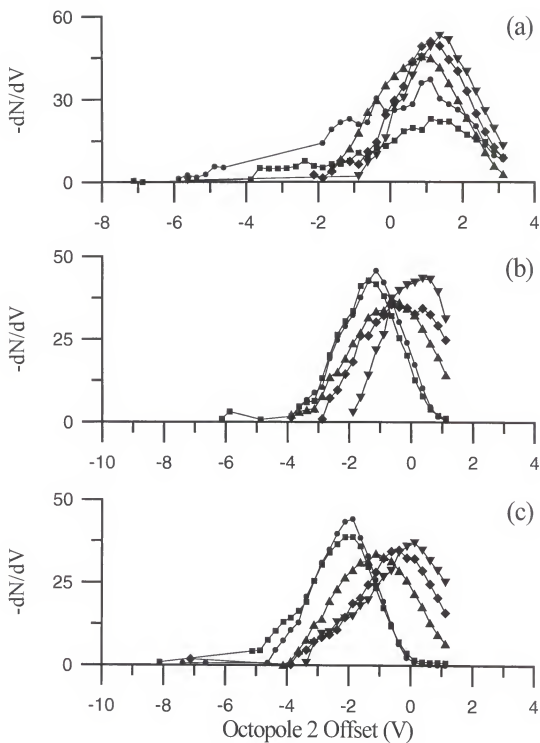


Figure 2-3 – First derivative of the stopping potential data shown in Figure 2-2. First derivative is shown for m/z 195.1 (●), m/z 524.3 (■), m/z 1222 (▲), m/z 1522 (◆), and m/z 1822 (▼). Shown for first octopole offsets, V_{O1} , of (a) +1 V, (b) -1 V, (c) -2 V, (d) -3 V, (e) -4 V, (f) -5 V, (g) -10 V, and (h) -20 V.

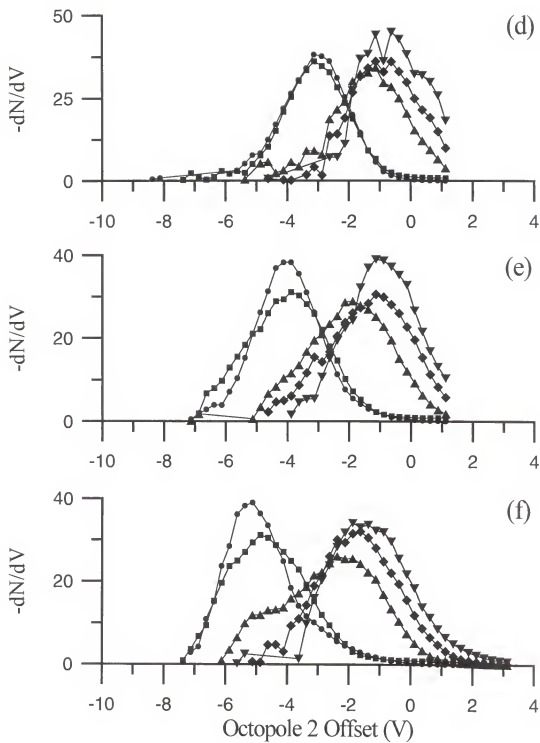


Figure 2-3 – continued.

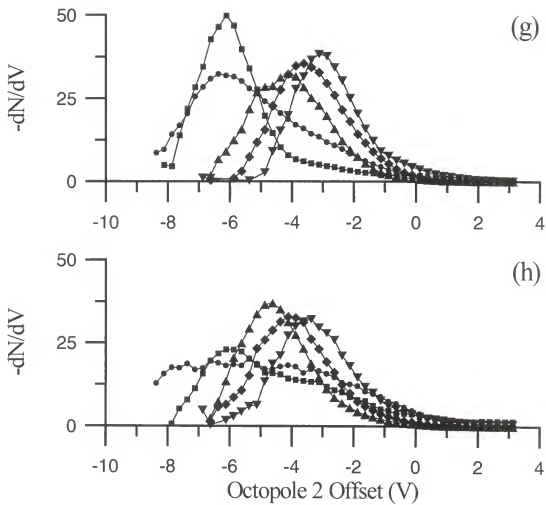


Figure 2-3 – continued.

the ion trap can be calculated as $E_{\text{Trap}} = z[V_{\text{O2Stop}} - V_{\text{TrapDC}}]$. If the kinetic energy distribution of ions entering the ion trap is desired, a slightly modified version of this same equation can be used to transform all of the data in the first derivative of the stopping potential curves. In that case, V_{O2Stop} would be replaced by the second octopole offset value in the x-axis of the stopping potential curves.

A few points can be made about the kinetic energy of the ion beam entering the ion trap. First, the ion beam has a relatively wide kinetic energy spread of approximately 2.5 eV at half of maximum. This was startling at first considering that electron ionization sources typically produce ion beams with kinetic energy spreads of only approximately 0.6 eV.⁵⁸ The wide kinetic energy spread from the electrospray ionization source can be attributed to the high pressure in the first octopole. A report in the literature showed that the kinetic energy distribution of an ion beam traveling through the collision cell of a triple quadrupole could be significantly broadened by collisions with several mtorr of gas.⁵⁴ Since the first octopole in the LCQ contained approximately 2 mtorr of air, this seemed like a reasonable explanation. The broadening is explained from a simple model that the kinetic energy variation of ions is proportional to $N^{1/2}$ where N is the number of collisions in the first octopole. Monte Carlo simulations of random collisions of ions suggested that in a 15 cm long collision cell filled with 1 mtorr argon, a 400 Da ion with a collision cross-section of $50.3 \text{ \AA}^2$ undergoes on average 2.6 collisions.⁵⁴ This translates to a collision profile of 2.6 ± 1.6 collisions or a spread of approximately $\pm 60\%$. This relatively large variation in the number of collisions for an ion beam produces a wide kinetic energy distribution.

The stopping potential curves also show that the kinetic energy of the ion beam varies as a function of both m/z and the first octopole offset. The average kinetic energy of the ions entering the ion trap can be plotted versus m/z (Figure 2-4). The plot shows that the kinetic energy of the ion beam increases with increasing m/z . If the kinetic energy of the ion beam were just a function of the offset voltages on the various ion optics, the kinetic energy should be constant with m/z . To develop an explanation, a theoretically based set of equations were derived for the kinetic energy of the ion beam at various points along the ion optics. The pressure in the source region and the heated capillary were assumed to be high enough that sufficient collisions occurred to damp any excess kinetic energy of the ions. The result is an ion beam which moves at the velocity of the viscous flow of the nitrogen in the heated capillary. As the ions exit the heated capillary they expand in a supersonic jet because of the pressure differential maintained across the small orifice by the mechanical pump.⁵⁹ The kinetic energy of the ion beam exiting the heated capillary, E_{OutCap} , can be represented by a simple constant velocity expansion model.

$$E_{\text{OutCap}} = \frac{1}{2}mv^2 \quad (2-1)$$

where v is the velocity of the nitrogen in the supersonic expansion. From here, the ions travel through the grounded skimmer cone and accelerate as they enter the first octopole to E_{InOI} .

$$E_{\text{InOI}} = \left[\frac{1}{2}mv^2 - zV_{\text{OI}} \right] \quad (2-2)$$

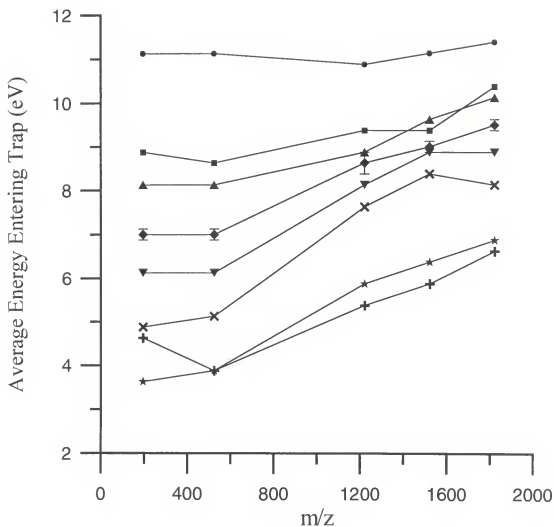


Figure 2-4 – Average kinetic energy of the ion beam entering ion trap derived from stopping potential measurements. Shown for various first octopole offsets of +1 V (●), -1 V (■), -2 V (▲), -3 V (◆), -4 V (▼), -5 V (✕), -10 V (✚), and -20 V (★). Error bars indicate one standard deviation.

From here ions drift through the first octopole; since the pressure is approximately 2 mtorr, a significant number of collisions can be assumed to occur. To account for these collisions, a collisional damping term can be added to equation 2-2.

$$E_{\text{OutO1}} = \left[\frac{1}{2} m v^2 - z V_{\text{O1}} \right] \alpha^N \quad (2-3)$$

$$\alpha = \frac{m^2 + m_{\text{Neutral}}^2}{(m + m_{\text{Neutral}})^2} \quad (2-4)$$

This damping term consists of α , the fraction of kinetic energy lost per collision, m_{Neutral} , the mass of the colliding neutral atom, and N , the total number of collisions.⁵⁴ From here, ions are accelerated briefly by the inter-octopole lens. This will be ignored since the ions then decelerate as they enter the second octopole such that their resulting kinetic energy is E_{InO2} .

$$E_{\text{InO2}} = \left[\frac{1}{2} m v^2 - z V_{\text{O1}} \right] \alpha^N - z [V_{\text{O2}} - V_{\text{O1}}] \quad (2-5)$$

The pressure in this second octopole is approximately 2×10^{-4} torr of helium, so it was assumed that the number of collisions in this device was negligible. Therefore, the kinetic energy out of the second octopole is the same as that into that octopole. Next, ions are accelerated as they enter the ion trap to a final kinetic energy, E_{Trap} .

$$E_{\text{Trap}} = \left[\frac{1}{2} m v^2 - z V_{\text{O1}} \right] \alpha^N - z [V_{\text{TrapDC}} - V_{\text{O1}}] \quad (2-6)$$

This can be rearranged and put in another form

$$E_{\text{Trap}} = \frac{1}{2} \alpha^N v^2 m - z V_{\text{TrapDC}} + z (1 - \alpha^N) V_{\text{O1}} \quad (2-7)$$

This equation, which was derived from a simple model of ion optics, predicts that the kinetic energy of ions entering the ion trap will be a function of the mass of the ion. This mass dependency results from the constant velocity expansion of the ions as they exit the heated capillary. From the pressure differential and the orifice size of the heated capillary, this supersonic jet velocity has been estimated as 780 m/s.⁵⁹

The other thing to note from equation 2-7 is that the kinetic energy of the ions is a function of the offset on the first octopole. Because of the high pressure in this device and the collisional damping term α^N , the first octopole offset does not cancel. The first octopole offset would cancel only if the number of collisions goes to zero. The data from Figure 2-4 can be plotted as a function of the first octopole offset to demonstrate more clearly this relationship (Figure 2-5). From this plot, an approximately linear relationship between average kinetic energy and the first octopole offset results for values of V_{O1} between -5 V and +1 V. This is what was predicted by equation 2-7. Although there are not enough data points to accurately solve for N and v , some qualitative conclusions can be drawn. The slope of the line relating E_{Trap} and V_{O1} is approximately 1 for m/z 195.1 and 524.3 (for V_{O1} between -5 V and +1 V). This implies that $\alpha^N \approx 0$; in other words, sufficient collisions occurred to almost completely damp the axial kinetic energy of these low mass ions. This relationship has been reported previously for triple quadrupole mass spectrometers which use a similar set of ion optics.⁵⁴ In that paper, ions were assumed to enter an RF-only quadrupole at the potential of the orifice (equivalent to the skimmer cone in the LCQ). These ions then accelerated to the offset on the quadrupole rods, but collisions moderated the kinetic energy of the ions to a few electron volts or less by the time the ions reached the end of the quadrupole. This makes the ions appear to be formed

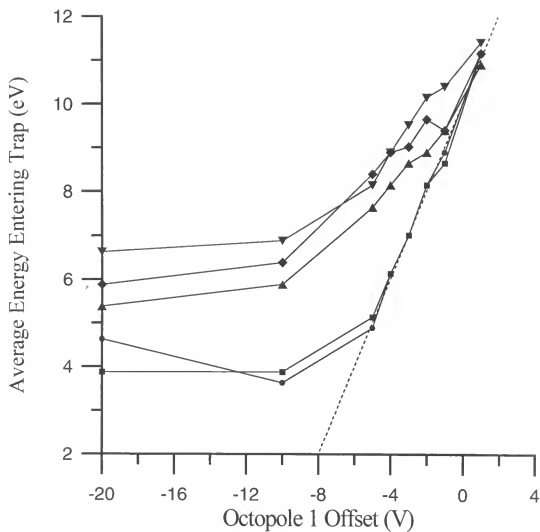


Figure 2-5 – Average kinetic energy of ion beam entering ion trap, E_{Trap} , derived from stopping potential measurements. Shown for various m/z ions 195.1 (●), 524.3 (■), 1222 (▲), 1522 (◆), and 1822 (▼).

at the offset potential of the quadrupole. This is the same thing which resulted in the LCQ for m/z 195.1 and 524.3, at least at higher first octopole offsets. The assumption is that at more negative first octopole offsets, the ions have so much kinetic energy as they drift through the octopole that not all of this kinetic energy can be damped. At the first octopole offsets typically used ($V_{O1}=-3$ V), however, the kinetic energy of the ions is almost completely damped and the ions reach almost thermal energies. This is significant because it suggests that some of the low mass ions may actually stop and be lost before they can be extracted by the inter-octopole lens. Higher mass ions do not lose as much kinetic energy because of the inefficiency with which high mass ions lose kinetic energy through collisions (see equation 2-4). This is shown in Figure 2-5 where the higher mass ions enter the ion trap with more kinetic energy than the lower mass ions, at a given first octopole offset.

Commercial Skimmer Stopping Potentials

Stopping potentials using the second octopole were next performed using the commercial skimmer cone design shown in Figure 2-1b. The design of the skimmer was changed by Finnigan MAT because of concerns over fringe field effects as ions enter the octopole. This commercial skimmer has a narrower ion exit side, which minimizes the penetration of the octopole RF field into the skimmer. The same type of stopping potential curves as before were performed, but for only a single first octopole offset of -3 V. The stopping potentials are shown in Figure 2-6a while the corresponding first derivatives are shown in Figure 2-6b. The most striking difference in these curves versus the ones shown for the prototype skimmer design is the different m/z ions have practically the same kinetic energy. A comparison of the kinetic energy of the ions as they enter the

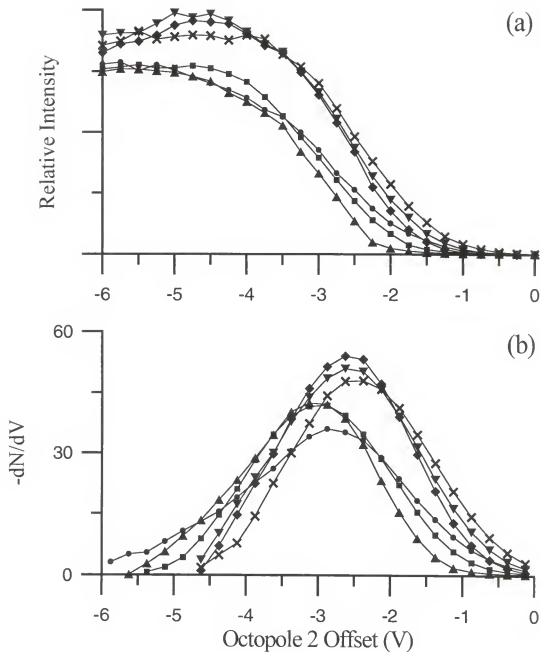


Figure 2-6 – Commercial skimmer design. (a) Stopping potentials generated with second octopole offset. (b) First derivative of the stopping potentials for m/z 106.1 (●), 195.1 (■), 524.3 (▲), 1222 (◆), 1522 (▼), and 1822 (×).

ion trap versus m/z is shown in Figure 2-7. The variation in kinetic energy of the ion beam from m/z 195.1 to 1822 is about 2.5 eV for the prototype skimmer design and only about 0.5 eV for the commercial skimmer design. Before, the constant velocity expansion in the supersonic jet was found to create a strong mass dependency in the kinetic energy of the ion beam (see Figure 2-4). One possible explanation for this can be given by returning to the theoretical model for the ion beam kinetic energy given in equation 2-7. The mass dependent term will disappear as either the velocity of the supersonic jet or the α^N collisional damping term approaches zero. Since the skimmer cone is identical on the side facing the heated capillary, the velocity of the jet has not changed. However, if something were to cause more collisions in the first octopole, this would increase N and the α^N term would decrease. Looking at the two skimmer designs shown in Figure 2-1, it is likely that the commercial skimmer cone has a much higher pressure in the region around the entrance to the octopole. The prototype skimmer had a much more open design which allowed more pumping out of this region. It is speculated that the higher pressure in the region of the exit side of the skimmer causes substantially more collisions to occur in the commercial skimmer design; therefore, most of the kinetic energy gained from the supersonic jet is collisionally damped. According to equation 2-7, as α^N approaches zero, the kinetic energy of the ions as they enter the ion trap approaches

$$E_{\text{Trap}} = z \left[V_{\text{OI}} - V_{\text{TrapDC}} \right] \quad (2-8)$$

In other words, the kinetic energy of the ion beam becomes independent of mass.

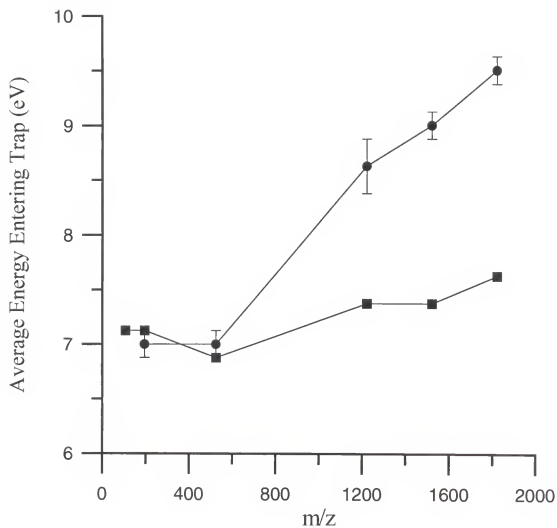


Figure 2-7 – Comparison of average kinetic energy of ions entering ion trap with prototype skimmer cone (●) and commercial skimmer cone (■). Error bars indicate $\pm$ one standard deviation from three replicate measurements.

Factors Which Affect Stopping Potential Measurements

These stopping potential measurements were performed under less than ideal circumstances. It is beyond the scope of this dissertation to describe all of the details of energy analyzers; several excellent reviews have been written on this topic.^{56,57} One underlying assumption of stopping potential measurements performed with an electrostatic analyzer which uses retarding fields is that the detection efficiency is not a function of ion beam kinetic energy. From a simple pseudopotential well model,¹⁴ the efficiency with which the ion trap can trap a given kinetic energy ion is a function of q_z . Changing the kinetic energy of the ions entering the ion trap will certainly affect the efficiency with which ions are trapped, complicating the interpretation of the stopping potential measurement. Therefore, the retarding potential used for the stopping potential measurements should be chosen so that the final kinetic energy of the ion beam as it enters the ion trap does not change. Referring back to equation 2-7, the kinetic energy of the ion beam as it enters the ion trap is a function of both V_{O1} and V_{TrapDC} ; therefore, these potentials would not be good choices for retarding potentials.

Another concern which arises from this discussion is the kinetic energy acceptance of the ion trap operated at a given q_z . If the ion beam has a wider kinetic energy distribution than the ion trap can trap at a given q_z , an incorrect kinetic energy distribution measurement will result. To address this, stopping potentials curves using the offset on the second octopole were generated for various q_z during injection values. It was reasoned that if a range of q_z values produced similar stopping potential measurements, the kinetic energy acceptance of the ion trap was larger than the kinetic energy distribution of the ion beam.

The first derivative of stopping potentials taken with different q_z during injection values for m/z 106.1 is shown in Figure 2-8. For q_z values between approximately 0.25 and 0.45, the measured kinetic energy distribution is approximately the same. This is consistent with the idea that the kinetic energy acceptance of the ion trap is greater than the kinetic energy spread of the ion beam. Similar results for m/z 1522 are shown in Figure 2-9. At the lower q_z values required for trapping of higher m/z ions, the kinetic energy acceptance of the ion trap appears to be narrower than the kinetic energy distribution of the ion beam. The ion trap is unable to trap the lower kinetic energy tail of the ion beam at higher q_z values. Although this result is not ideal, for a range of q_z values from 0.05 to 0.11 the measured center of the kinetic energy distribution remains the same. The consequence of the narrower energy acceptance seems to be an inaccurate measurement of the lower kinetic energy tail of the ion beam rather than the average kinetic energy.

The plots shown in Figure 2-8 and Figure 2-9 are the first such curves known to be reported. Some interesting manipulations of these data can be made. If one integrates the measured kinetic energy distribution at each q_z , a plot of the total number of ions (of all kinetic energies) trapped at each q_z results. The stopping potential measurements at each q_z provide information on the kinetic energy acceptance at each q_z . The kinetic energy acceptance of the ion trap can be a limiting factor when trying to measure the true kinetic energy distribution of an ion beam. Another possible manipulation is to integrate over all q_z values; this might allow the true kinetic energy distribution of the ion beam, independent of q_z , to be constructed. But even up to m/z 1522, a q_z value near the middle

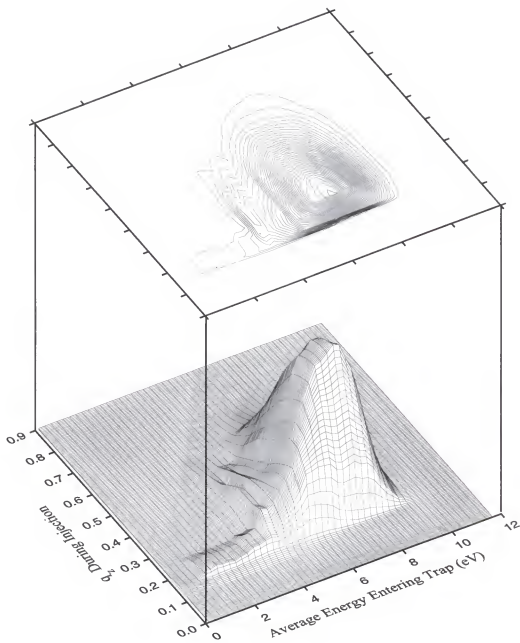


Figure 2-8 – Surface plot (with contour plot shown above) of the first derivative of several stopping potential curves measured with different q_z during injection values. Shown for m/z 106.1. These data were taken with the commercial skimmer.

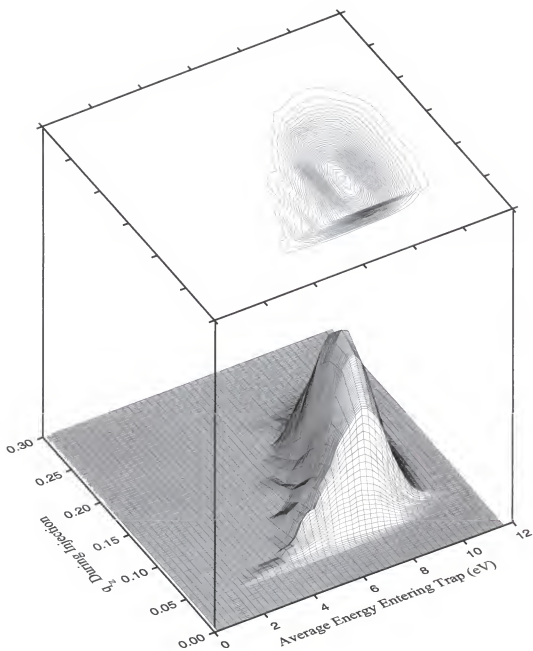


Figure 2-9 – Surface plot (with contour plot shown above) of the first derivative of several stopping potential curves measured with different q_z during injection values. Shown for m/z 1522. These data were taken with the commercial skimmer.

of the acceptance will provide a reasonable approximation of the true kinetic energy distribution.

Effect of q_z on Ion Injection Efficiency

Up to this point, the kinetic energy distribution has been measured and the effect of q_z on the efficiency of ion injection has been inferred. It was seen that at certain q_z values, no ions of a given m/z were trapped. In this section, the effect of q_z on the efficiency of ion injection will be investigated further. The goal was to determine if the optimum q_z could be predicted for a given m/z or range of m/z ions. All of these experiments were performed with the prototype skimmer, but many of the techniques used and described are applicable to the commercial skimmer.

Up until now, the RF voltage on the ring electrode has been expressed as the reduced parameter q_z . However, q_z is proportional to the RF voltage divided by the m/z of interest. This means for a given RF voltage, different m/z ions are being injected at different q_z values. Therefore, it makes more sense to describe the RF voltage as LMCO which is independent of the m/z of the ion. A series of experiments was performed where the LMCO during injection was varied and the relative intensities of various m/z ions were recorded. The results for four different m/z ions are shown in Figure 2-10. The data were run through a seven-point running average smoothing algorithm twice to eliminate any fine structure so that the basic shape of the curves could be seen more clearly. In Chapter 3, unsmoothed data will be shown and some of the fine structure in the data discussed. Several things can be noted from the data in Figure 2-10. First, there is an optimum LMCO for each m/z ion; this optimum increases as a function of m/z . Second,

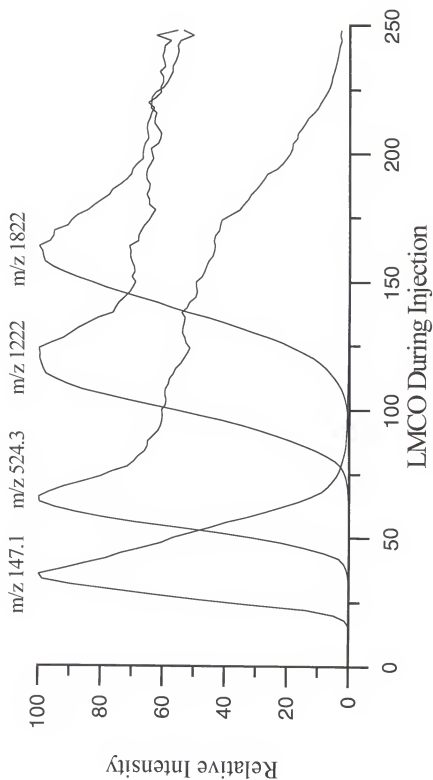


Figure 2-10 – Experimental variation in trapping efficiency as a function of the LMCs during injection.

as the m/z is increased the range of efficient LMCO values increases as the right hand tail grows. Third, it is not possible to efficiently trap a wide range of m/z ions with a single LMCO value. The rest of this chapter is devoted to determining if the optimum LMCO can be predicted and to investigate methods of trapping a wide m/z range of ions for a full scan experiment.

Predicting the Optimum Ring RF Voltage to Trap Ions

In 1989, two articles appeared which suggested a possible relationship between the optimum LMCO for injection and m/z .^{29,43} Louris *et al.* used four different m/z ions to suggest that the optimum q_z is proportional to $m^{-1/2}$ (optimum LMCO is proportional to $m^{1/2}$).²⁹ On the other hand, McLuckey *et al.* used seven different m/z ions and concluded that $LMCO \propto m$.⁴³ To further investigate this discrepancy, the effect of the LMCO value used during injection was recorded for the 30 different m/z ions shown in Table 2-1; the results are shown in Figure 2-11. This plot is rather confusing because of the number of m/z ions shown. However, if the optimum LMCO for each ion is plotted versus m/z , a clear relationship results (Figure 2-12). The optimum LMCO was chosen as the LMCO which resulted in the largest relative intensity. Fitting a straight line to these data produces the equation

$$LMCO = 0.0742 \cdot (m / z) + 26.8 \quad (2-9)$$

For a given m/z ion, the optimum LMCO can be predicted using this equation. A few +2 and +3 ions were included and do not deviate from this relationship. This relationship can also be plotted in terms of the optimum q_z for each m/z , as shown in Figure 2-13. Fitting a line to these data produces

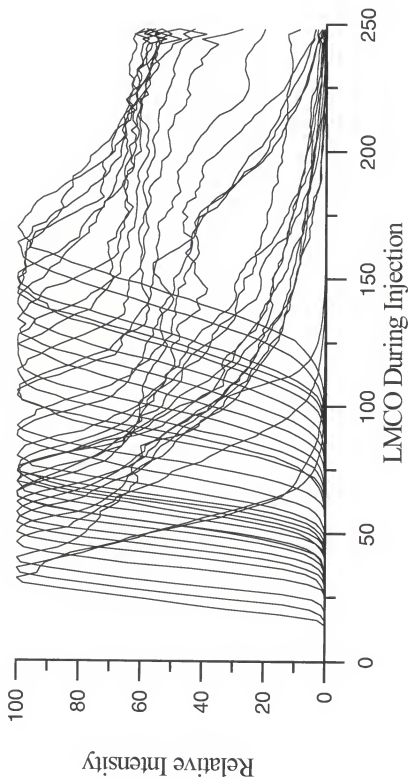
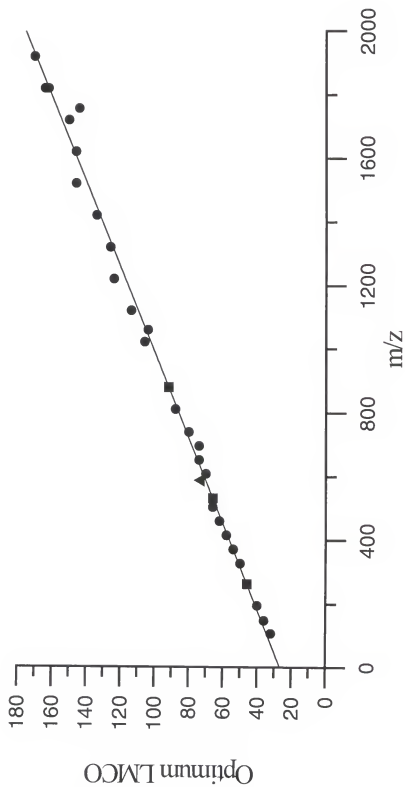


Figure 2-11 – Experimental variation in trapping efficiency as a function of the LMC0 during injection for the 30 m/z ions listed in Table 2-1.



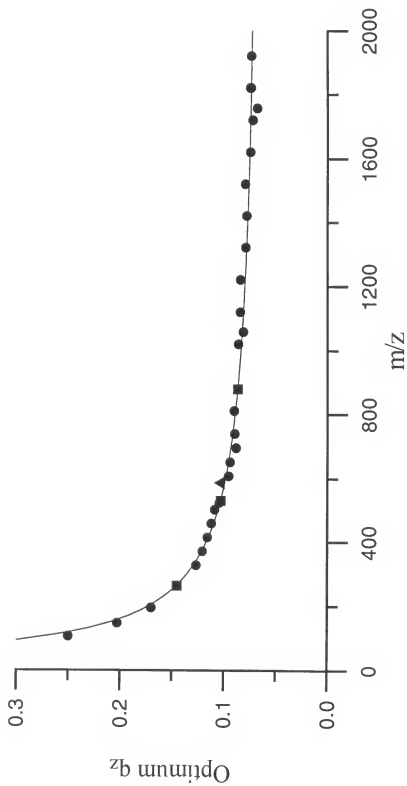


Figure 2-13 – Plot of the optimum q_z during injection for all of the ions in Figure 2-11 as a function of m/z . $z=+1$ (●), $z=+2$ (■), and $z=+3$ (▲). Line is best fit from equation 2-10.

$$q_z = 0.0615 + \frac{22.2}{m/z} \quad (2-10)$$

Although the data are relatively convincing, a theoretical basis for the linear relationship shown in equation 2-9 would be comforting. To develop such a relationship, the pseudopotential well model was revisited.

The pseudopotential well model was originally developed in 1968 by Major and Dehmelt.³² It uses a simple approximation ignoring the higher-order frequency components of ion motion, reducing the ion trap to a simple harmonic oscillator.¹⁴ This simple motion can be represented by

$$Z(t) = z_{\max} \cdot \sin(\omega_z t) \quad (2-11)$$

where $Z(t)$ is the position in the axial direction, $z_{\max}$ is the maximum amplitude of oscillation, and ω_z is the frequency of oscillation which can be calculated using the approximation which is valid for $q_z < 0.4$

$$\beta_z^2 = a_z + \frac{q_z^2}{2} \quad (2-12)$$

where

$$\omega_z \equiv \frac{\beta_z \Omega}{2} \quad (2-13)$$

The maximum axial excursion an ion can have and remain within the ion trap is z_0 .

Substituting this into equation 2-11 and then taking the first derivative to compute the velocity of the ion

$$\dot{Z}(t) = z_0 \cdot \cos(\omega_z t) \quad (2-14)$$

which can also be written

$$\dot{z}(t) = \frac{z_o q_z \Omega}{2\sqrt{2}} \cdot \cos\left(\frac{\beta_z \Omega}{2} t\right) \quad (2-15)$$

The maximum velocity is of most interest and occurs when $\cos(\beta_z \Omega t/2) = 1$.

$$\dot{z}_{\max}(t) = \frac{z_o q_z \Omega}{2\sqrt{2}} \quad (2-16)$$

Converting this velocity to kinetic energy

$$E_{\max} = \frac{m z_o^2 q_z^2 \Omega^2}{16} \quad (2-17)$$

which can be rearranged

$$q_z = \frac{4}{z_o \Omega} \sqrt{\frac{E_{\max}}{m}} \quad (2-18)$$

and written in terms of LMCO

$$\text{LMCO} = \frac{4}{q_{ej} z_o \Omega} \sqrt{\frac{E_{\max} m}{z^2}} \quad (2-19)$$

In the case of the commercial skimmer cone and the approximate kinetic energy distribution given by equation 2-8, the dependency is predicted to be

$$\text{LMCO} = \frac{4}{q_{ej} z_o \Omega} \sqrt{\left[V_{OI} - V_{\text{TrapDC}}\right] \left(\frac{m}{z}\right)} \quad (2-20)$$

In other words, since the kinetic energy of the ion beam is approximately constant, the LMCO should be proportional to $(m/z)^{1/2}$. However, experimentally the optimum LMCO was found to be proportional to the m/z (see equation 2-9 and Figure 2-12). Since these experiments were performed with the prototype skimmer, the mass-dependent kinetic energy shown in equation 2-7 can be plugged into equation 2-19.

$$\text{LMCO} = \frac{4}{q_{\text{ej}} z_o \Omega} \sqrt{\frac{1}{2} \alpha^N v^2 \left(\frac{m}{z}\right)^2 + \left[(1 - \alpha^N) V_{\text{OI}} - V_{\text{TrapDC}}\right] \left(\frac{m}{z}\right)} \quad (2-21)$$

This equation predicts the experimentally observed linear relationship between LMCO and m/z when the second, m/z , term is small.

The simple pseudopotential well model allowed a theoretical explanation to be given to the experimental behavior seen relating the optimum injection RF level to the m/z . As mentioned before, the pseudopotential well model is only an approximation and cannot be used to predict quantitatively the experimental observation. It was however useful in supporting the decision to fit a linear relationship between LMCO and m/z . Although the optimum LMCO during injection can now be accurately predicted, the use of a single (optimum) LMCO is only useful when injecting ions of a single m/z . The next section addresses the simultaneous injection of ions of varying m/z .

Trapping a Wide m/z Range of Ions

In many experiments it is critical to inject ions of more than a single m/z . Since each choice of LMCO only efficiently traps a relatively narrow range of m/z ions (see Figure 2-10), it would seem logical that the use of multiple LMCO values during the injection stage would permit the trapping of a wider m/z range. However, the number of stages and the LMCO values to use for each stage must be judiciously chosen. As an example, the conditions necessary to trap ions for a full scan mass spectrum covering m/z 100 to 2000 were investigated. As a starting point, the LMCO during injection was stepped between three values (LMCO=36, 66, and 150) with an equal amount of time at each. The relative trapping efficiency of 22 different m/z ions (bradykinin, renin substrate, and three of the ions from polyethylene glycol were excluded) was calculated.

In other words, the intensity of each of these m/z ions obtained from the stepped injection scheme was compared to the maximum intensity obtained if the entire injection event was spent at the LMCO predicted by equation 2-9 for that m/z . A plot of the measured trapping efficiency versus m/z is shown in Figure 2-14. The first thing to note is m/z 106.1 was not trapped at all; this is a result of stepping the LMCO during injection from the lowest to the highest value. The low m/z ions trapped during the first steps can be ejected if their m/z is below the LMCO used in the last step. One way around this is to start at the highest LMCO and step backward toward the lowest LMCO. This avoids the problem of ions being ejected which are below the LMCO. However, as the LMCO during injection is lowered, the high m/z ions will be stored at lower and lower q_z values. Practically, ions are not stored efficiently at q_z values below approximately 0.03 meaning ions above approximately m/z 1100 will not remain in the ion trap. As a result, it is not always possible to trap and store a wide range of m/z ions. When trying to trap ions all the way out to high m/z , starting at the lowest LMCO value will usually yield the best results. On the other hand, if very low m/z ions are desired, it may be advantageous to start at the highest LMCO value.

Another point to note from Figure 2-14 is that several peaks and valleys in trapping efficiency are observed. Referring back to the curves shown in Figure 2-11, the spikes occur when multiple LMCO values efficiently inject a given m/z ion; on the other hand, valleys occur when not enough LMCO values are concentrated to inject a given m/z ion. Variations in trapping efficiency with m/z will distort ion ratios and are undesirable; sharp variations may even distort isotope ratios. It is therefore advantageous to optimize the injection levels used to minimize the variation in trapping efficiency with m/z . The

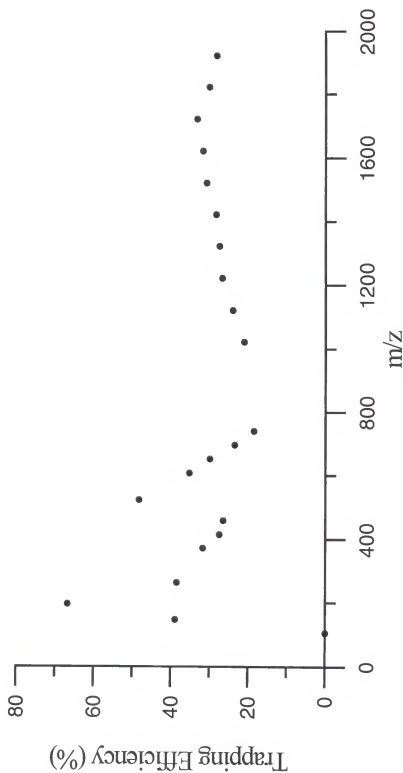


Figure 2-14 – Measured trapping efficiency for ion injection with 1/3 of injection time spent at LMCO values of 36, 66, and 150 which correspond to the optimum values for the injection of m/z 124, 528, and 1660, respectively. Efficiency shown relative to 100% of time spent at optimum LMCO for each m/z.

experiment shown in Figure 2-14 was not trivial and it is not practical to test every combination of injection levels in this way.

It may be possible to predict the trapping efficiency using the data for the 30 m/z ions shown in Figure 2-11. These data are normalized to 100% indicating the maximum trapping efficiency for that m/z. At a given LMCO, the height of each m/z curve is the relative trapping efficiency. When working with multiple LMCO injection levels, the height of each m/z curve at each LMCO value should be multiplied by the fraction of time spent (1/3 in the case of three equal injection periods) and the height of each m/z curve summed for all LMCO values. The trapping efficiencies predicted by this method can be compared to the values obtained in Figure 2-14, as shown in Figure 2-15 (note that all thirty m/z ions are shown for the predicted trapping efficiency). The agreement is quite good and discrepancies are easily explained because of the experimental variation obtained when generating the curves shown in Figure 2-11. This technique should make it possible to optimize the LMCO injection levels off-line in a much more efficient manner.

A Visual Basic program was written in Microsoft Excel which tried various combinations of LMCO injection levels and determined the trapping efficiency variation with m/z. A figure of merit was assigned to the trapping efficiency variation so that the program could automatically determine the optimum set of LMCO values. For simplicity, it was decided to minimize the peak-to-peak variation in trapping efficiency, defined as

$$\eta_{pp} = \frac{\eta_{\max} - \eta_{\min}}{\eta_{\text{average}}} \cdot 100\% \quad (2-22)$$

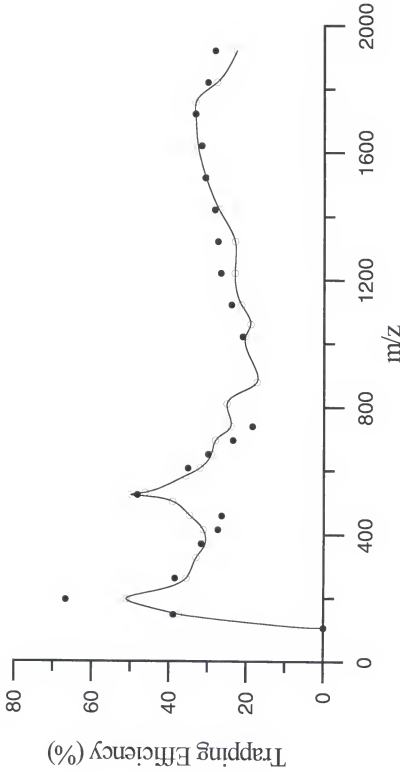


Figure 2-15 – Trapping efficiency for ion injection with 1/3 of injection time spent at LMCO values of 36, 66, and 150 which correspond to the optimum values for the injection of m/z 124, 528, and 1660, respectively. Measured trapping efficiency from Figure 2-14 (●). Predicted trapping efficiency (○). Efficiency shown relative to 100% of time spent at optimum LMCO for that m/z.

where η is the trapping efficiency at each m/z relative to spending 100% of the injection time at the optimum LMCO for that m/z . Beginning with a scan range of m/z 106.1 to 1922, the program tried all possible LMCO combinations of 1, 2, 3, and 4 injection levels. The set of LMCO values which minimized η_{pp} for each number of injection levels is shown in Figure 2-16. The peak-to-peak trapping efficiency, η_{pp} , variation decreases as the number of injection levels is increased (228%, 118%, 75.2%, and 59.6%). As more injection levels are used, the m/z range of interest is more adequately covered. Five injection levels were not attempted because the program was expected to take approximately 250 hours to execute. However, this program predicted that using the four LMCO injection levels of 38, 78, 118, and 166 provided the lowest variation in trapping efficiency across the mass range of m/z 106.1 to 1922 (note that no ions below m/z 166 will be trapped). Using equation 2-9, the m/z these LMCO values most efficiently inject can be calculated and are shown as vertical lines in Figure 2-16. This type of analysis was performed on other scan ranges to determine an equation to predict the LMCO values to use for a given scan range. This was done for fourteen other scan ranges of various widths; m/z 106.1 to 1022 is shown in Figure 2-17 and m/z 1022 to 1922 is shown in Figure 2-18.

From all of the scan ranges it was found that, as one would expect, larger scan ranges required more injection levels to prevent the efficiency from varying to a large extent. On the other hand, if too many injection levels were used for short scan ranges, the average efficiency suffered. The results for various scan ranges are shown in Table 2-2, with the resulting values of $\eta_{average}$ and η_{pp} shown for various numbers of injection levels. If possible, the minimum number of injection levels which produced a η_{pp} less

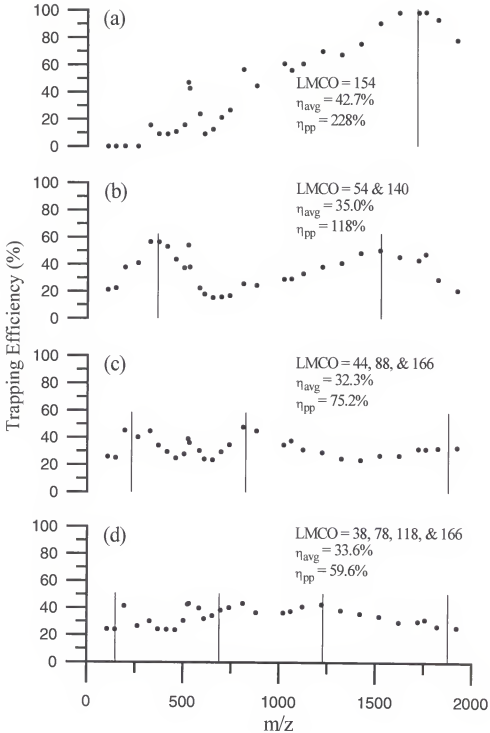


Figure 2-16 – Predicted trapping efficiency for scan range of m/z 106.1 to 1922. LMCO values shown for minimum η_{pp} . (a) 1 injection level, (b) 2 injection levels, (c) 3 injection levels, (d) 4 injection levels.

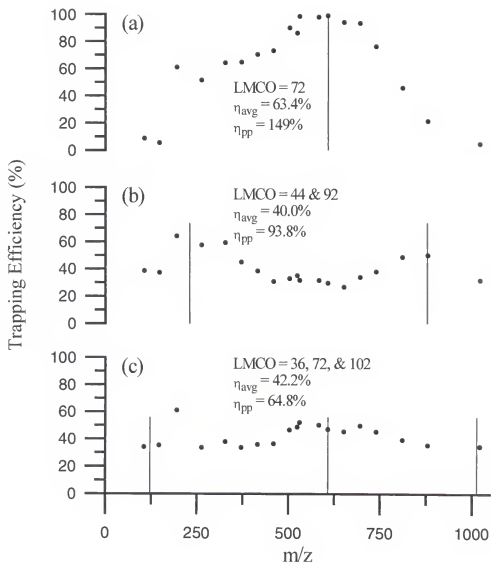


Figure 2-17 – Predicted trapping efficiency for scan range of m/z 106.1 to 1022. LMCO values shown for minimum η_{pp} . (a) 1 injection level, (b) 2 injection levels, (c) 3 injection levels.

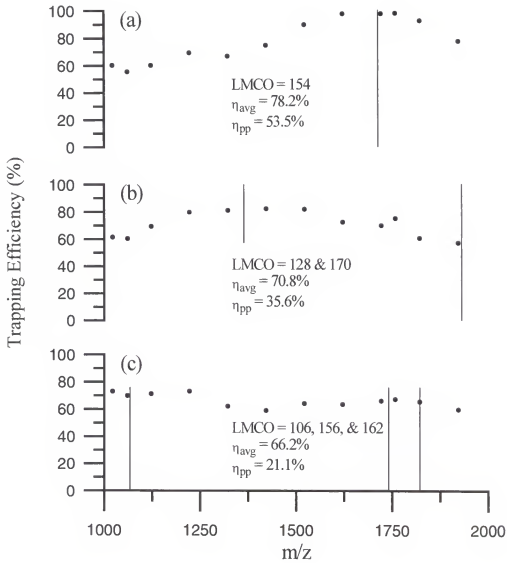


Figure 2-18 – Predicted trapping efficiency for scan range of m/z 1022 to 1922. LMCO values shown for minimum η_{pp} . (a) 1 injection level, (b) 2 injection levels, (c) 3 injection levels.

Table 2-2 – Results of computer optimization of injection levels for various scan ranges. The number of injection levels shown in bold was chosen as the optimum for that particular scan range.

First m/z	Last m/z	# Injection Levels	η_{average} (%)	η_{pp} (%)
106.1	1922	1	42.7	228.0
		2	35.0	118.0
		3	32.3	75.2
		4	33.6	59.6
106.1	1022	1	63.4	149.0
		2	40.0	93.8
		3	42.2	64.8
1022	1922	1	78.2	53.5
		2	70.8	35.6
		3	66.2	21.1
608.4	1822	1	60.5	131.0
		2	47.0	58.9
		3	48.4	35.0
106.1	503.3	1	73.5	78.7
		2	60.3	52.0
		3	61.6	43.8
503.3	1022	1	70.1	65.6
		2	60.6	27.7
1022	1522	1	83.1	38.9
		2	71.3	20.3
696.4	1222	1	75.8	49.8
		2	70.1	31.3
1422	1922	1	89.3	25.5
		2	86.9	21.3
1522	1922	1	92.7	13.5
		2	92.2	12.1
106.1	327.2	1	81.2	31.0
		2	77.3	24.5
327.2	530.8	1	89.1	30.6
		2	86.0	21.9
811.5	1122	1	86.1	20.6
		2	82.0	15.5
1122	1522	1	91.0	21.0
		2	85.2	11.7
530.8	811.5	1	87.8	29.5

than approximately 30% was chosen for each scan range. This criterion prevented more injection levels from being used than were necessary. In choosing the number of injection levels, more were needed for larger scan ranges and scan ranges at lower m/z values. Since the range of LMCO values which results in efficient trapping for low m/z ions is less than that for higher m/z ions (see Figure 2-11), more injection levels are needed to cover the same m/z range located at lower m/z .

In order to develop an equation to predict the optimum number of injection levels to use for a scan range, a two-parameter system was chosen. The first parameter is a measure of the width of the scan range, while the second is related to whether the scan range is at low or high m/z . Two parameters were defined as

$$x_1 = \frac{(\text{Last } m/z) - (\text{First } m/z)}{2000} \quad (2-23)$$

$$x_2 = \frac{(\text{First } m/z) + (\text{Last } m/z)}{2 \cdot 2000} \quad (2-24)$$

where (First m/z) and (Last m/z) are the first and last m/z in the scan range. Essentially, these are reduced parameters which define the width of the scan range and its center. These parameters were calculated for all of the scan ranges; the results are shown in Table 2-3. A multivariate linear regression was performed using an equation of the form

$$\text{Optimum \# Levels} = m_1 \cdot x_1 + m_2 \cdot x_2 + b \quad (2-25)$$

where m_1 and m_2 are slopes and b is the y-intercept. The linear regression produced $m_1=4.28$, $m_2=-1.2$, $b=1.18$, with an $r^2=0.785$. The slopes and y-intercept were rounded off to $m_1=4.5$, $m_2=-1$, and $b=1.2$ since there was no particular significance to the extra digits. The values were inserted into equation 2-25; the result was rounded off to the nearest integer to produce the predicted number of injection levels shown in Table 2-3.

Table 2-3 – Results of the equation used to predict the optimum number of injection levels given the desired scan range. The number of levels is predicted from the reduced parameters x_1 and x_2 .

First m/z	Last m/z	x_1	x_2	Optimum # Levels	Predicted # Levels
106.1	1922	0.908	0.507	4	5
106.1	1022	0.458	0.282	3	3
1022	1922	0.450	0.736	3	2
608.4	1822	0.607	0.608	3	3
106.1	503.3	0.199	0.152	3	2
503.3	1022	0.259	0.381	2	2
1022	1522	0.250	0.636	2	2
696.4	1222	0.263	0.480	2	2
1422	1922	0.250	0.836	1	1
1522	1922	0.200	0.861	1	1
106.1	327.2	0.111	0.108	1	2
327.2	530.8	0.102	0.215	1	1
811.5	1122	0.155	0.483	1	1
1122	1522	0.200	0.661	1	1
530.8	811.5	0.140	0.336	1	1

$$\text{Predicted \# Levels} = \text{ROUND}(4.5 \cdot x_1 - x_2 + 1.2) \quad (2-26)$$

Although not 100% accurate in its prediction, this equation does a relatively good job. For the widest scan range of m/z 106.1 to 1922, equation 2-26 suggests 5 injection levels which is probably better than 4, although the data are not available. At this point, an equation has been derived to predict the number of injection levels to use given only the scan range; however, the actual injection levels to use must still be chosen.

To determine the injection levels to use for a given scan range, the computer optimized injection levels were sorted based on the number of injection levels which was determined to be optimum. Table 2-4 shows the scan ranges for which only a single injection level was necessary along with the corresponding optimum injection level. This optimum injection level is the m/z which is calculated from the LMCO with equation 2-9. It makes sense that the optimum injection level is near the center of the scan range, since choosing a LMCO which efficiently injects the m/z at the center of the scan range should also cover surrounding m/z ions. It was assumed that the optimum injection level would always occur at a particular point within the scan range. As a result, the fraction of the scan range was calculated using the following equation

$$\text{Fraction of scan range} = \frac{(\text{Injection Level}) - (\text{First } m/z)}{(\text{Last } m/z) - (\text{First } m/z)} \quad (2-27)$$

It was found that different scan ranges had optimum injection levels which occurred at approximately the same fractions of the scan range. The same process was used for scan ranges which were determined to need two (Table 2-5), three (Table 2-6), and four (Table 2-7) injection levels. In each case the average fraction of the scan range was calculated for each injection level.

Table 2-4 – Optimum injection level shown for a series of scan ranges. The fraction of the scan range is the fractional position of the injection level in the scan range.

First m/z	Last m/z	Injection Level 1	Fraction of Range
1422	1922	1714	0.584
1522	1922	1768	0.615
106.1	327.2	230	0.560
327.2	530.8	473	0.715
811.5	1122	986	0.563
1122	1522	1337	0.538
530.8	811.5	716	0.660
		Average	0.605

Table 2-5 – Two optimum injection levels shown for a series of scan ranges. The fraction of the scan range is the fractional position of the injection level in the scan range.

First m/z	Last m/z	Injection Level 1	Fraction of Range	Injection Level 2	Fraction of Range
503.3	1022	743	0.462	1013	0.983
1022	1522	1175	0.306	1499	0.954
696.4	1222	851	0.294	1175	0.911
		Average	0.354	Average	0.949

Table 2-6 – Three optimum injection levels shown for a series of scan ranges. The fraction of the scan range is the fractional position of the injection level in the scan range.

First m/z	Last m/z	Injection Level 1	Fraction of Range	Injection Level 2	Fraction of Range	Injection Level 3	Fraction of Range
106.1	1022	122	0.017	608	0.548	1013	0.990
1022	1922	1067	0.050	1741	0.799	1822	0.889
608.4	1822	608	0.000	1337	0.600	1741	0.933
106.1	503.3	122	0.040	392	0.720	446	0.856
		Average	0.027	Average	0.667	Average	0.917

Table 2-7 – Four optimum injection levels shown for a single scan range. The fraction of the scan range is the fractional position of the injection level in the scan range.

First m/z	Last m/z	Injection Level 1	Fraction of Range	Injection Level 2	Fraction of Range	Injection Level 3	Fraction of Range	Injection Level 4	Fraction of Range
106.1	1922	149	0.024	689	0.321	1229	0.618	1876	0.975
		Average	0.024	Average	0.321	Average	0.618	Average	0.975

From these fractions and equation 2-26, a novel algorithm was written which could predict the number of injection levels and the actual injection levels to use given only the scan range. Some minor adjustments were made to the fractions used with four injection levels, but otherwise the values were taken directly from Table 2-4, Table 2-5, Table 2-6, and Table 2-7. These adjustments did not change the results dramatically because there were a wide range of optimum levels which produced efficient trapping across the mass range when four levels were used. However, by lowering the last level from 97.5% to 85%, the last LMCO value is lowered allowing lower m/z ions to remain in the ion trap. This algorithm, `calcionrf()`, is an ITCL (ion trap control language) function⁵¹ written for the LCQ which takes two inputs, the first m/z and last m/z of the scan range (see Figure 2-19). The number of injection levels, `numofionrfs`, is calculated and the values for these injection levels are stored in an array, `msrfmass[0,1,2,3]`. The chosen injection levels can be represented graphically as vertical lines at particular points within the scan range (see Figure 2-20). Essentially, the optimum injection levels are spaced throughout the scan range.

As a test of the `calcionrf()` function, full scan spectra for a mixture of polyethylene glycol polymers were acquired. This mixture produces a series of ions from approximately m/z 177 to 1576. Such a mixture should show a smooth distribution of ions; any drastic fluctuations in trapping efficiency across the m/z range will produce an uneven distribution. Spectra were taken over different scan ranges to determine if the algorithm could calculate appropriate injection levels to use under varying circumstances. An example of the kind of spectra obtained using the algorithm is shown in Figure 2-21a.

```

/* calcionrf() -- Sets full scan injection levels */

/*      Information used:
      ARG1=firstmass, ARG2=lastmass, max # of injection levels to use
Returns:
      numofionrfs      = # of injection levels to use for scan range
      msrffmass[0-->(numofionrfs-1)] = the injection levels
*/
local i,first;

/* Calculate numofionrfs needed */
numofionrfs= 1.2 + 4.5*(ARG2-ARG1)/highestmass - 1*(ARG1+ARG2)/(2*highestmass);
numofionrfs=FLOOR(numofionrfs+.5);
numofionrfs=MAX(numofionrfs,1); // Don't allow less than 1 ion RFs
numofionrfs=MIN(numofionrfs,4); // Don't allow more than 4 ion RFs

/* Calculate msrffmass[] */
// Setup rftime array based upon numofionrfs calculated
i=0;
repeat(numofionrfs)
{
    rftime[i]=1/numofionrfs;
    i+=1;
}
// Find msrffmass
if (numofionrfs==1)
    msrffmass[0]=(ARG2-ARG1)*0.6 + ARG1;
else if (numofionrfs==2)
{
    msrffmass[1]=(ARG2-ARG1)*0.95 + ARG1;
    first=MAX(mtoionrf(msrffmass[1]),ARG1); // Reset first mass to LMCO of highest msrffmass
    msrffmass[0]=(ARG2-first)*0.35 + first;
}
else if (numofionrfs==3)
{
    msrffmass[2]=(ARG2-ARG1)*0.92 + ARG1;
    first=MAX(mtoionrf(msrffmass[2]),ARG1); // Reset first mass to LMCO of highest msrffmass
    msrffmass[1]=(ARG2-first)*0.67 + first;
    msrffmass[0]=(ARG2-first)*0.03 + first;
}
else if (numofionrfs==4)
{
    msrffmass[3]=(ARG2-ARG1)*0.85 + ARG1;
    first=MAX(mtoionrf(msrffmass[3]),ARG1); // Reset first mass to LMCO of highest msrffmass
    msrffmass[2]=(ARG2-first)*0.55 + first;
    msrffmass[1]=(ARG2-first)*0.32 + first;
    msrffmass[0]=(ARG2-first)*0.03 + first;
}
return(numofionrfs);

```

Figure 2-19 – calcionrf() ITCL function for computing the number of injection levels (numofionrfs) and the injection level for each (msrffmass[0,1,2,3]). The only inputs are the first and last m/z of the desired scan range.

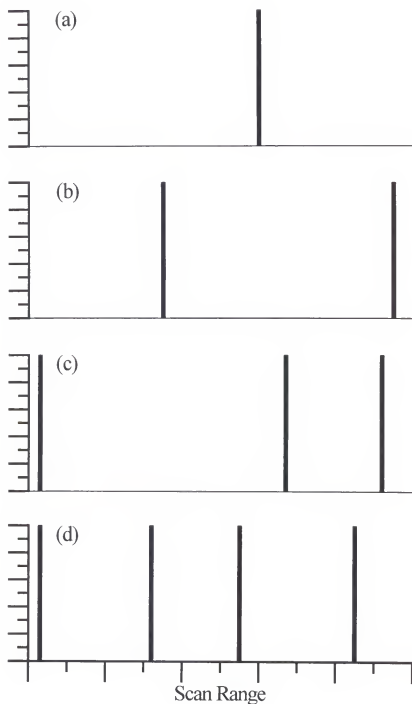


Figure 2-20 – Graphical representation of the injection levels chosen by algorithm for a given scan range. Vertical bars indicate relative positions of injection levels within scan range. Shown for (a) one, (b) two, (c) three, and (d) four injection levels.

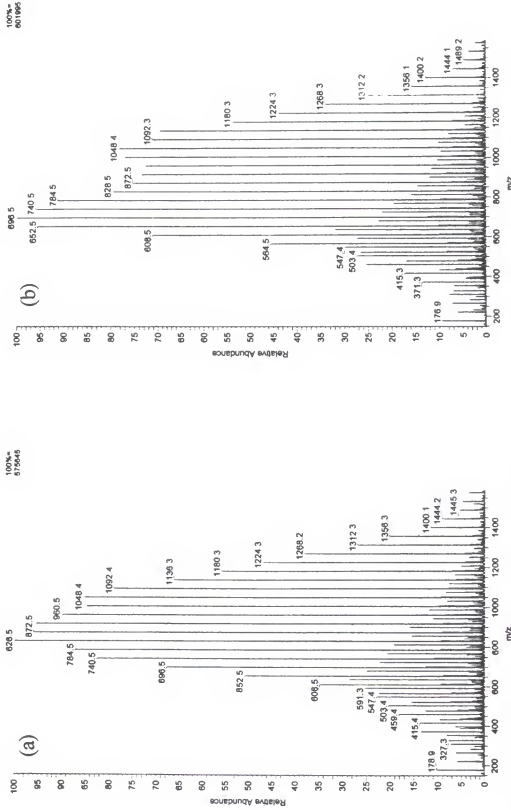


Figure 2-21 – Spectra of polyethylene glycol polymer mixture showing a scan from m/z 150 to 1600. (a) 4 injection levels set to m/z 193.5, 614, 947.5, and 1382.5 (LMCO = 41, 72, 97, and 129) calculated using calcmrff. (b) Slightly different set of injection levels set to m/z 193.5, 614, 1049, and 1556.5 (LMCO = 41, 72, 105, and 142) showing decreased trapping efficiency near m/z 900.

For comparison, if the injection levels are not chosen as judiciously, a spectrum such as that shown in Figure 2-21b results showing decreased trapping efficiency around m/z 900.

From what has been shown so far, wider m/z ranges can be obtained by using more injection levels. The ultimate limit of this is to ramp the LMCO during injection rather than using a series of discrete values. In fact, it should be possible to construct a non-linear ramp which varies the LMCO during injection in such a way to produce a flat trapping efficiency across the m/z range. Since low m/z ions are trapped over a narrower range of LMCO values, the non-linear ramp would spend more time trapping lower m/z ions. For now, the algorithm which was developed provides a good starting point for more sophisticated techniques of varying the RF level during injection. An important question remains how ions are trapped in the first place; this is the subject of Chapter 3.

CHAPTER 3 SIMULATIONS OF ION INJECTION

Introduction

In Chapter 2, experimental studies of ion injection into the ion trap of a Finnigan MAT LCQ LC/MSⁿ mass spectrometer with an electrospray ionization source were described. From these experiments, the LMCO during injection was found to affect dramatically the efficiency with which injected ions were trapped. A simple pseudopotential well model was used to qualitatively model the relationship between the optimum LMCO and m/z ; however, this model was inadequate for quantitatively predicting the optimum LMCO. In addition, the pseudopotential well model could not predict the shape of the relative intensity versus LMCO curves (see Figure 2-10) which are important in choosing the LMCO levels for injecting a wide m/z range of ions.

A more complex model was needed; in this chapter, the first large scale computer simulations of ion injection into a quadrupole ion trap are shown. Using SIMION v6.0, ion trajectories of injected ions were calculated to determine what values of experimental parameters resulted in successfully trapped ions. Ion injection simulations reported in the literature have always started ions at the endcap boundary,^{41,53,60} however, SIMION provides the ability to start ions outside the ion trap and more accurately simulate what happens experimentally. In fact, SIMION simulations in this chapter of ions injected from outside the ion trap produce very different results than SIMION simulations of ions

started at the endcap boundary. This is attributed to RF field penetration through the endcap hole. As a test of the accuracy of the computer simulations, the results were compared to experimental ion injection data. With good agreement, the computer simulations were used to develop a model of how injected ions are trapped. The better understanding provided by the model of the processes involved in trapping ions has led to techniques to improve trapping efficiency.

History of Quadrupole Ion Trap Simulations

Trapping ions from continuous ionization sources such as electrospray has been shown to be relatively inefficient, with less than 5% of the total ions being trapped.^{40,43} This low efficiency was explained by computer simulations which showed that ions were only trapped over a small range of RF phases.^{53,61} However, the process by which injected ions are trapped is still not well understood. In Chapter 1, equations of motion for ions in an ion trap were presented; from these the trajectories of ions can be calculated. This is one basis of computer simulations which are powerful tools for studying ion motion inside the ion trap. One assumption of the potential equations presented in Chapter 1 is that the field inside the ion trap is purely quadrupolar. However, practical ion traps have a perturbed field because the electrodes do not extend infinitely as well as because of machining tolerances, assembly tolerances, and endcap holes which introduce higher-order multipole field components.⁶² In addition, the Finnigan MAT ion traps use a “stretched” electrode geometry^{24,25} which introduces weak, even order multipoles. A specially designed simulation program is needed to simulate

ion motion in an ion trap with these higher-order fields superimposed on the main quadrupole field.^{62,63}

In Chapter 1, the potential within the ion trap was solved for a pure quadrupole field (see equation 1-8). This potential equation can be modified to include contributions from higher-order field components.⁶⁴

$$\begin{aligned}\Phi(r, z) = A_0 + A_1 z + A_2 \left(\frac{1}{2} r^2 - z^2 \right) + A_3 z \left(\frac{3}{2} r^2 - z^2 \right) \\ + A_4 \left(\frac{3}{8} r^4 - 3r^2 z^2 + z^4 \right) + \dots\end{aligned}\quad (3-1)$$

where the A_n terms with $n=0, 1, 2, 3$, and 4 correspond to the monopole, dipole, quadrupole, hexapole, and octopole components, respectively. Because this potential equation cannot be represented in closed form, it cannot be solved implicitly. As a result, a numerical integration technique such as finite-element analysis or finite-difference analysis is necessary to calculate the potential within the ion trap. Several groups have developed computer simulations of ion trajectories which can solve these potential equations which include higher-order fields. The use of finite-element analysis to study quadrupole ion traps was first reported in 1989.⁶⁵ A finite-element calculation was performed to generate a map of the potential within the ion trap. To study the motion of ions, an interpolative look-up algorithm was used to calculate the potential at the current position of the ion and the potential around it. These interpolated potentials were then scaled with a cosine function to model the dynamically varying RF potential. A fourth-order Runge-Kutta routine was then used to integrate the acceleration expression derived from the Lorenz equation. The resultant velocity expression was then integrated to obtain position.⁶⁵

Franzen and co-workers' nonlinear ion trap simulation has been used to simulate ion traps with different percentages of higher-order fields.^{62,66} The nonlinear ion trap simulation was used to simulate ion injection (with the ions started at the endcap boundary) including the effect of higher buffer gas pressure.⁶⁰ March and co-workers developed the field interpolation method (FIM) to simulate ion traps which contain higher-order fields and monopole and which employ dipole resonant excitation.^{67,68} The ion trap simulation program ITSIM, developed by Cooks and co-workers, is a multiparticle simulation which calculates the potentials in the ion trap by the multipole expansion of the Legendre polynomials.⁶⁹⁻⁷¹ This technique also allows the simulation of ion trap geometries which include percentages of higher-order fields. It has been used to study many different modes of ion trap operation including ion injection.⁴¹ All of these simulations allow higher-order fields (e.g., hexapole and octopole) to be included as percentages of the main quadrupole field. However, they all require that the percentage of higher-order fields be entered explicitly; they also require that the ions be started within the ion trap.

For a given electrode geometry it can be very complicated to calculate the percentages of the different higher-order fields.⁶⁶ As a result, March and co-workers have an expanded version of their FIM simulation that can simulate any electrode geometry given the equations for the surfaces of the electrodes.⁶⁷ However, the only one of these simulation programs which can model endcap holes is the finite-element analysis program developed by Lunney and co-workers.⁶⁵ Holes in the endcap electrodes are necessary for ions to enter the ion trap and then exit to be detected. Only a simulation that allows the potential in the ion trap to be calculated from any arbitrary electrode

surface geometry (not just continuous equations) can accurately simulate the effects of endcap holes. The endcap holes distort the RF field in a relatively complex manner which cannot be modeled simply by superimposed higher-order fields.⁷² For many simulations, the effect of the endcap holes may be negligible; however, when ions are injected into the ion trap and therefore have large axial trajectories, the holes may be very important. The only published ion injection simulations to include endcap holes studied the effect of damping voltages on ions started at the plane of an endcap.^{7,65} In this chapter, the first large scale ion injection simulations were performed to further study the effect of endcap holes.

Ion Injection Simulations using SIMION v6.0

To model the effect of endcap holes, a simulation which does not require the electrodes to be represented by equations was needed. SIMION v6.0 (Idaho National Engineering Laboratory, Idaho Falls, ID) was chosen because it is a commercially available ion optics simulation program which is flexible enough to adequately model the quadrupole ion trap. SIMION allows electrodes to be simply gridded point by point. The potential at each point is then calculated using an over-relaxation finite difference technique; these potentials are then used to calculate the electric field gradient and the force on the ion. The position and velocity of the ion at the next time step is calculated using a fourth-order Runge-Kutta numerical integration.

The LCQ electrodes (as shown in Figure 3-1) were input into SIMION on an 800 by 800 grid; this was the largest workspace possible for the 120 MHz Pentium computer with 32 megabytes of RAM that was used. The inherent rotational symmetry of the ion



Figure 3-1 – SIMION electrode grid of the LCQ ion trap including a portion of the second octopole modeled as a cylindrical tube lens. This grid is 40 mm by 80 mm.

trap made it necessary to input only the top half of the electrodes shown in Figure 3-1 into this grid; the full three-dimensional ion trap was created through a solid rotation of this grid. Each grid square corresponded to 0.05 mm by 0.05 mm. Finnigan MAT mechanical drawings of the electrodes provided exact dimensions of the ion trap including the equations for the hyperbolic electrode surfaces, which were input directly into SIMION. Portions of the exit lens and the second octopole were also gridded. In order to maintain cylindrical symmetry and save memory, the octopole was modeled as a cylindrical tube lens. The electrodes were refined using an iteration limit of 50,000, an over-relaxation factor of 0.90, a historical memory factor of 0.70, and a convergence objective of 5×10^{-6} . The default computational quality of 2 was used unless otherwise noted. A user program was written which allowed RF and DC voltages to be applied to the ring electrode.

A one-dimensional Monte Carlo hard-sphere collision model was incorporated into the user program to simulate the random collisions with helium buffer gas. In this collision model, the distance an ion traveled before colliding, ℓ , was calculated using the following equation:⁵⁴

$$\ell = -\frac{\ln(1-\zeta)}{\sigma n} \quad (3-2)$$

where ζ is a random number between 0 and 1, σ is the collision cross-section of the ion, and n is the number density of the buffer gas. Once the ion had traveled this randomly determined distance, it was assumed to have a collision. In this one-dimensional model, the ion's kinetic energy was reduced using the following equation:

$$E' = E \cdot \frac{m^2 + m_{\text{He}}^2}{(m + m_{\text{He}})^2} \quad (3-3)$$

where E and E' are the kinetic energies before and after the collision, respectively, m is the mass of the ion, and m_{He} is the mass of a helium atom. The random distance to the next collision was then calculated and the process repeated. By reseeding the random number generator, a different collision sequence is produced. Using different random number generator seeds for a series of injected ions, statistical information was obtained on the percentage of ions which were trapped. In these studies, ten ions were injected at each set of conditions with different random number generator seeds. Studies with larger populations did not yield significantly different results.

Collisions were assumed to occur at all spatial locations including outside the ion trap. This is in contrast to the LCQ ion trap where the pressure of helium inside the ion trap is approximately ten times higher than outside. Unless otherwise noted, a simulated pressure of 1.5 mtorr helium ($n=4.8 \times 10^{13} \text{ cm}^{-3}$) was used. The collision cross-section, σ , of the ion provides some measure of the size of the ion. A few papers have been published giving values for collision cross-sections of ions; from these a value of $50 \text{ \AA}^2$ was chosen for m/z 100 ions colliding with helium atoms.^{55,73-75} For simulations of other m/z ions, the following equation was used to calculate the collision cross-section of any m/z ion relative to a m/z 100 ion. The equation is based on the assumptions that the ions are spherical and of equal density.

$$\sigma = 50 \left(\frac{m}{100} \right)^{\frac{2}{3}} \quad (3-4)$$

where m is the mass of the ion whose collision cross-section is to be calculated. For example, a m/z 1522 ion would have a collision cross-section of $307 \text{ \AA}^2$ or approximately six times that of a m/z 100 ion. This value was rounded off to $300 \text{ \AA}^2$ and used for all simulations of m/z 1522 ions.

Simulations of Ion Trajectories

For the first set of ion injection experiments, ions were started at the inner plane of the entrance endcap electrode as in all previously reported simulations. The ions had an initial position of $z_{\text{init}}=z_0=7.85 \text{ mm}$, $x_{\text{init}}=0 \text{ mm}$, and $y_{\text{init}}=0 \text{ mm}$ (see Figure 3-2). The ions were given an initial kinetic energy, E_0 , at an angle, Θ , measured from the z -axis. An example of a typical trajectory simulation is shown in Figure 3-3 for a m/z 100 ion. This ion was started at the endcap with $E_0=7 \text{ eV}$ and $\Theta=5^\circ$ at a q_z of 0.2. Besides the q_z value, the phase of the RF voltage on the ring electrode at the time the ion is started is known to be very important in determining the fate of an injected ion.^{53,61} The initial RF phase, ϕ_{RF} , was defined by the relationship $V \cdot \sin(\Omega t + \phi_{\text{RF}})$. For this work, ϕ_{RF} varied between -180° and $+180^\circ$. When ions were started at a ϕ_{RF} of -180° , 0° , or 180° , the voltage applied to the ring is initially 0 V; at $\phi_{\text{RF}}=90^\circ$, the voltage is at a maximum (+V), and at $\phi_{\text{RF}}=-90^\circ$ the voltage is at a minimum (-V). The ion shown in Figure 3-3 was started at a ϕ_{RF} of -30° . The ion begins at the entrance endcap and therefore with a large axial excursion. Collisions with helium atoms at 1.5 mtorr randomly occur; the time of the collision and amount of kinetic energy lost per collision is shown at the bottom of Figure 3-3. A percentage of the ion's kinetic energy is lost in each collision (see equation 3-3) so the amount of kinetic energy lost varies with the instantaneous kinetic energy of

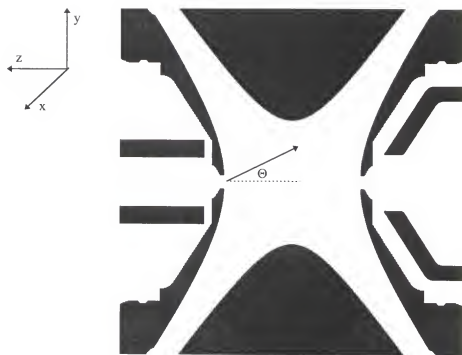


Figure 3-2 – Close-up view of SIMION grid defining starting position of ions at the plane of the entrance endcap. Origin (0,0,0) is located at the center of the ion trap.

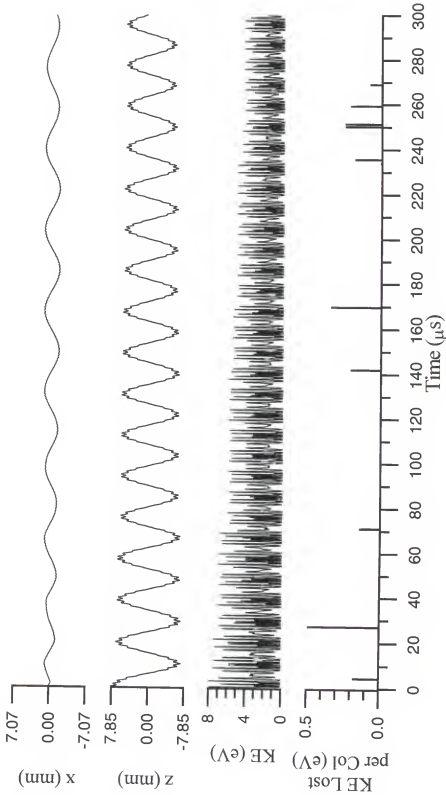


Figure 3-3 – Ion trajectory simulation of m/z 100 ion. Ion was started at the plane of the entrance endcap at $z_{\text{init}}=7.85$ mm and $x_{\text{init}}=y_{\text{init}}=0$ mm with 7 eV of kinetic energy. $\Theta=5^\circ$; $q_z=0.2$; $\phi_{\text{RF}}=30^\circ$. The kinetic energy lost per random collision is shown on the bottom trace for a simulated helium pressure of 1.5 mtorr. This ion was trapped indefinitely because of the initial conditions and the collisional damping.

the ion. Over the course of the simulation, a steady damping of the kinetic energy and axial excursion of the ion is observed, resulting in an ion which is trapped indefinitely.

This ion was lucky, however; it suffered enough collisions early on to stabilize its trajectory. Since the collisions are random, the random number generator in the computer simulation can be reseeded to obtain a different random collision sequence. By injecting a population of ions with different collision sequences, statistics on the trapping efficiency of a particular combination of experimental parameters can be obtained. In this chapter, the effect of different experimental parameters on trapping efficiency will be studied.

Ion Injection Simulations of m/z 100 Ions

Effect of Endcap Holes on Ion Injection

To determine the effect of endcap holes, two different SIMION electrode grids were refined. The first grid included one hole (0.060 in) in each endcap electrode, while the second did not have holes in either endcap. The parameters which were predicted to have the largest influence on ion injection were the q_z during injection and the initial RF phase; in addition, the effect of the injection angle, Θ , was also studied. Previous ion injection simulations have shown that larger injection angles produce more efficient trapping.^{36,53,76-78} Ions were again started at the inner plane of the entrance endcap electrode ($z_{\text{init}}=z_0=7.85$ mm, $x_{\text{init}}=0$ mm, and $y_{\text{init}}=0$ mm). To determine an appropriate initial kinetic energy, E_0 , measurements of stopping potentials with the commercial skimmer for m/z 106.1 were used. From these measurements shown in Chapter 2, the average kinetic energy of m/z 106.1 ions entering the ion trap was 7 eV. For the

following simulations, an initial kinetic energy, E_o , of 7 eV was used. Experimentally, ions of m/z 100 were predicted to be efficiently trapped when injected at a q_z of approximately 0.25 for an ion trap offset, V_{TrapDC} , of -10 V. Using this q_z during injection, ten ions were injected at each initial RF phase between 0° and 359° in 1° increments to determine the percentage of ions trapped at each phase. An ion was considered to be trapped if it underwent a stable trajectory for at least 400 μs without being lost to an electrode surface or an endcap hole. Monitoring ions for longer times increased the simulation time but did not produce significantly different results. A plot of the percentage of ions trapped at each RF phase is shown in Figure 3-4a for $\Theta=5^\circ$. It was found that ions which were started at RF phases around 52° and -50° were successfully trapped; however, no ions were trapped at other RF phases. This partially explains the low trapping efficiency of externally produced ions from continuous ionization sources since ions are only trapped if they arrive in the ion trap at a small range of RF phases.

Other injection angles ($\Theta=0^\circ, 5^\circ, 10^\circ, 15^\circ, 20^\circ, 30^\circ$, and 45°) were also studied. Based on these simulations, some general observations can be made. At an injection angle of 0° , ions which arrived at RF phases which allowed them to enter the ion trap tended to travel straight through and out the opposite endcap hole. Conversely, ions injected at angles of 20° and larger had significant amounts of radial kinetic energy and often hit the ring electrode. Ions with angles larger than 30° often had insufficient axial kinetic energy to penetrate more than 1 mm into the ion trap before being turned around into the entrance endcap electrode. To compare the effect of different Θ angles quantitatively, the total number of ions trapped over all RF phases was summed and divided by the total number of ions injected over all RF phases, in this case (360 phases)

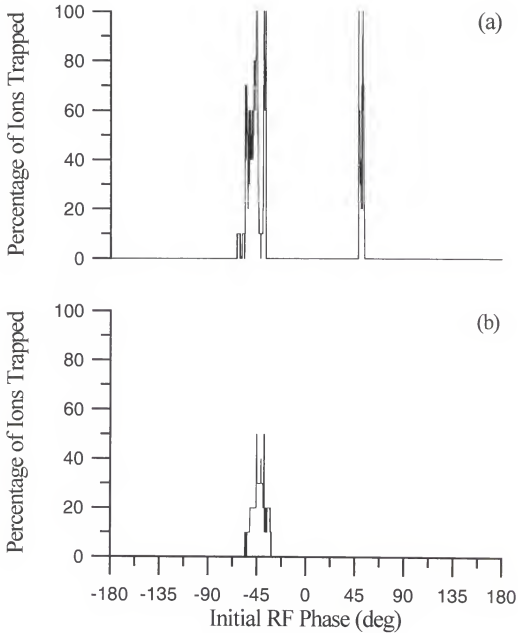


Figure 3-4 – Effect of endcap holes on the percentage of ions trapped as a function of initial RF phase. Ions of m/z 100 started at the inner plane of the entrance endcap ($z_{\text{init}}=z_0=7.85$ mm, $x_{\text{init}}=0$ mm, and $y_{\text{init}}=0$ mm) with $E_0=7$ eV and $\Theta=5^\circ$; simulated helium pressure of 1.5 mtorr; $q_z=0.25$. Simulation (a) with and (b) without endcap holes.

$\times (10 \text{ ions/phase}) = 3,600 \text{ ions}$. At the most efficient angle, $\Theta=5^\circ$, 3.6% of the ions were trapped; thus, this injection angle was used for subsequent simulations of m/z 100.

The other point to note from Figure 3-4a is that there are two ranges of RF phases for which efficient trapping of ions is observed. This is in contrast to previous simulations^{41,60} which predict trapping only at the phase range around -50° . This discrepancy was puzzling at first, but close examination of the ion trajectories at these two sets of RF phases revealed that the endcap holes played a significant role in ion trapping. Since the distorted field caused by the endcap holes was not accounted for by previous simulations, this seemed a probable explanation. To test this hypothesis, the simulation grid which omitted the endcap holes was used and the simulations repeated using the same conditions as in Figure 3-4a; the results are shown in Figure 3-4b. Without endcap holes, only one range of RF phases resulted in efficient trapping, as observed in previous simulations. Also, the efficiency with which ions are trapped at these phases is only about half as much without endcap holes as with endcap holes.

It was not clear if the extra range of efficient phases around 52° was just an artifact of the initial position of the ions in these simulations. At initial RF phases between 0° and 180° , the voltage on the ring is initially positive; ions are initially pushed back toward the endcap and without an endcap hole strike the endcap. When endcap holes were included in the model, the ions can sometimes back up into the hole without being lost until the voltage on the ring swings negative.⁷ The simulations were repeated for ions started 0.5 mm inside the endcap electrode; the results are shown in Figure 3-5. As before, ions were trapped over two ranges of RF phases when endcap holes were included and only one range of RF phases with no endcap holes. The RF phases which

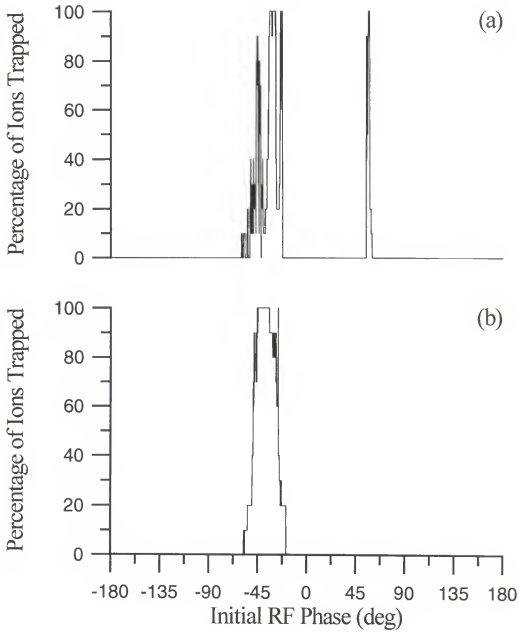


Figure 3-5 – Effect of endcap holes on the percentage of ions trapped as a function of initial RF phase. Same conditions as Figure 3-4 except ions started 0.5 mm closer to the center of the ion trap at $z_{\text{init}}=7.35$ mm. Simulation (a) with and (b) without endcap holes.

produced efficient trapping shifted to higher RF phases when the ions were started closer to the center of the ion trap. Also, starting the ions closer to the center increased the overall efficiency of trapping, particularly for the no-hole case, since ions were trapped over a wider range of RF phases. To understand the role of the endcap holes, a closer investigation of the ion trajectories at various RF phases is necessary.

Figure 3-6 shows the trajectories of ions started 0.5 mm inside the ion trap (with and without endcap holes) at six different initial RF phases using the same conditions as in Figure 3-5. For these simulations, a computational quality of 15 was used instead of the default of 2. This improved the accuracy of the numerical integration but took about five times longer to simulate. The axial positions of the ions are plotted versus time and the corresponding voltage applied to the ring is shown with the trajectory of each ion (see Figure 3-6). Figure 3-6a shows $\phi_{RF}=20^\circ$ which corresponded to the voltage on the ring starting and remaining positive at the beginning of the simulation; this caused the ions to turn around and be lost either through the endcap hole or into the endcap electrode. In Figure 3-6b, with $\phi_{RF}=56^\circ$, the voltage on the ring was again positive and the simulation without endcap holes showed the ion being lost to the electrode. However, with endcap holes present the ion was not lost. Equipotential contours near the endcaps indicated that the hole created a weaker RF trapping field. This trapping field was just weak enough to prevent the ion from being repelled back out the entrance endcap hole; rather, the ion stayed in the ion trap and was successfully trapped. In Figure 3-6c, with $\phi_{RF}=70^\circ$, the ion is initially repelled toward the entrance endcap because the voltage on the ring electrode is positive. However, before the ion reaches the endcap (whether or not the hole is present), the voltage on the ring decreases to zero (at $\phi_{RF}=180^\circ$) and then becomes

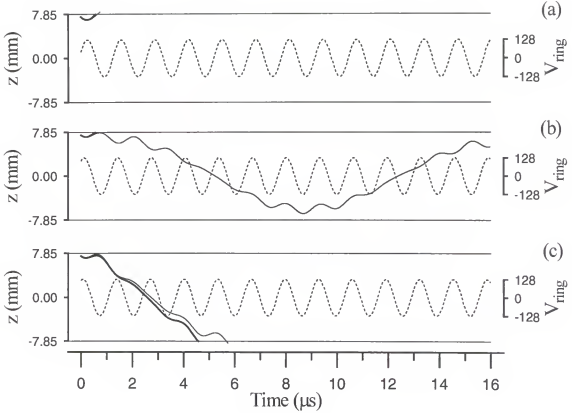


Figure 3-6 – Simulated trajectories of ions started 0.5 mm inside the ion trap with (thin solid line) or without (thick solid line) endcap holes for six different initial RF phases, ϕ_{RF} . Ions of m/z 100 started just inside entrance endcap ($z_{init}=7.35$ mm, $x_{init}=0$ mm, $y_{init}=0$ mm) with $E_0=7$ eV and $\Theta=5^\circ$; simulated helium pressure of 1.5 mtorr; $q_z=0.25$; $z=+7.85$ mm corresponded to the entrance endcap and $z=-7.85$ mm corresponded to the exit endcap; the corresponding voltage on the ring electrode (V_{peak}) is shown as the dotted line. (a) $\phi_{RF}=20^\circ$, ions are repelled toward entrance endcap. (b) $\phi_{RF}=56^\circ$, for the simulation with holes the ion is not lost back to the entrance endcap because of the weak RF field near the hole. (c & d) $\phi_{RF}=70^\circ$ and -70° , respectively, ions gain enough kinetic energy and strike the exit endcap. (e) $\phi_{RF}=-30^\circ$, ions are trapped with or without holes. (f) $\phi_{RF}=-21^\circ$, ions are only contained with the stronger RF field created by not having an endcap hole.

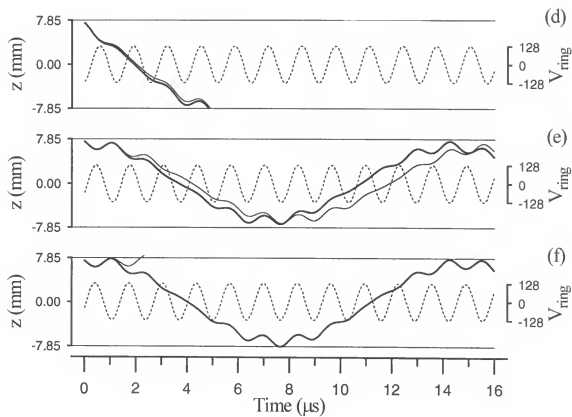


Figure 3-6 – continued.

negative after 0.40 μs , at which time the ion is accelerated toward the center of the ion trap. As the voltage on the ring continues to oscillate between positive and negative, the ion gains sufficient axial kinetic energy to fly straight through the ion trap and strike the exit endcap or exit through the endcap hole. Figure 3-6d shows an ion with a similar fate to that in Figure 3-6c, except the ion was started when the voltage on the ring was initially negative ($\phi_{\text{RF}}=-70^\circ$) and therefore accelerated toward the center of the ion trap. These ions also fly straight through the ion trap and strike the exit endcap. Figure 3-6e shows $\phi_{\text{RF}}=-30^\circ$ where the voltage on the ring is initially slightly negative and ions are attracted toward the center of the ion trap. However, the voltage on the ring quickly swings positive and the ions are decelerated sufficiently to contain them in the ion trap and thus are trapped. Figure 3-6f shows another discrepancy between ion trajectories with and without holes. In contrast to $\phi_{\text{RF}}=56^\circ$, at $\phi_{\text{RF}}=-21^\circ$ the weak RF trapping field near the endcap hole causes the ion in the simulation with holes to be lost, while the stronger field created without holes is able to contain the ion. Although Figure 3-6 only shows ion trajectories for six RF phases, the fate of ions started at all RF phases between -180° and $+180^\circ$ is summarized in Figure 3-5.

The plots shown in Figure 3-4 and Figure 3-5 show which RF phases result in efficient trapping of ions started at or near the endcap. However, these plots are for a specific q_z and therefore are only slices through a more complex surface mapping the percentage of ions trapped at various RF phases and q_z values. Next, both the initial RF phase and the q_z during injection were varied. The q_z was varied from 0 to 0.9 in increments of 0.005 while the initial RF phase was varied from 0° to 359° in 1° increments. At each combination, ten ions were injected with different random number

generator seeds for the collision model simulating a pressure of 1.5 mtorr of helium. The ions were started at the plane of the entrance endcap ($z_{\text{init}}=z_0=7.85$ mm) with the same initial conditions as in Figure 3-4a. The data were plotted in a series of contour plots in Figure 3-7 where the z-axis is the percentage of the population of ten ions which were trapped. Darker areas indicate regions where more ions were trapped. Figure 3-7a shows that without endcap holes, there is only one range of RF phases at any q_z for which ions are efficiently trapped; however, the RF phase shifts and the width of the range of phases changes as a function of q_z . The results of including endcap holes are shown in Figure 3-7b. Here, the combinations of q_z and initial RF phase which resulted in efficient trapping showed a bullet-shaped trend. The two ranges of RF phases for which ions are trapped become closer together as the q_z during injection is lowered until they converge around $q_z=0.16$, below which the RF trapping field is too weak to trap any ions.

These results indicated that the effects caused by the weakened RF field near the endcap holes are crucial to understanding injected ions. One effect of the holes is to alter the potential the ions experience near the endcap; this is shown graphically in Figure 3-8 and Figure 3-9. Without endcap holes, an ion started at the inner plane of the entrance endcap starts at the potential of the endcap, which in our case was -10 V. This is not the case, however, when holes are cut into the endcap electrodes. The potential in the center of the hole is not fixed, but varies as a function of the voltage on the ring electrode. With the hole in the endcap electrode, the field from the ring electrode bulges out the endcap hole (see Figure 3-9). This means that the potential at the inner plane of the endcap electrode in the region of the hole will not be -10 V, the offset voltage on the ion trap. When the voltage on the ring electrode is initially negative (as in Figure 3-9a), ions which

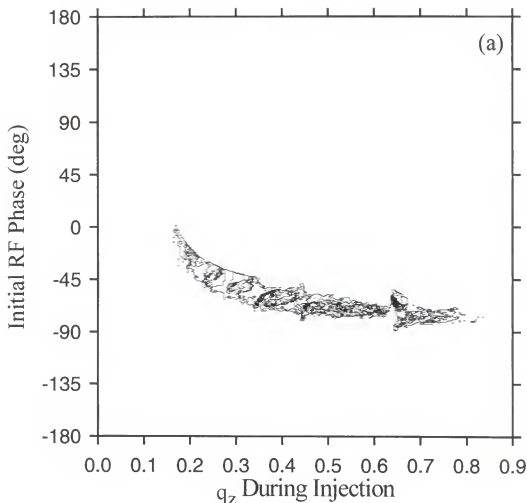


Figure 3-7 – Contour plots of the percentage of ions trapped as a function of RF phase and q_z for m/z 100 ions; simulated helium pressure of 1.5 mtorr. (a) No holes in endcaps and ions started at the inner plane of the entrance endcap ($z_{\text{init}}=7.85$ mm, $x_{\text{init}}=0$ mm, $y_{\text{init}}=0$ mm, and $\Theta=5^\circ$) with $E_0=7$ eV. (b) Holes in endcaps and ions started under the same conditions as in (a). Each of these simulations took over 5 days to complete.

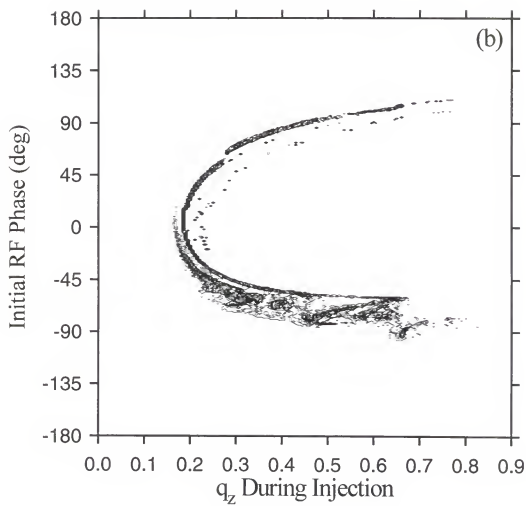


Figure 3-7 – continued.

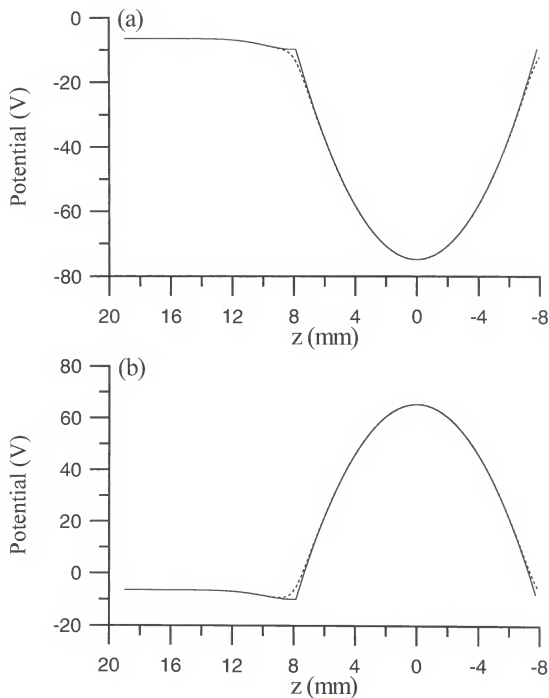


Figure 3-8 – Potential ions experience with (dotted line) and without (solid line) endcap holes at different z positions; $x=y=0$ mm. (a) Ring electrode voltage is -100 V; for m/z 100 at a $q_z=0.25$ this corresponds to an RF phase of -51° . (b) Ring electrode voltage is +95 V; for m/z 100 at a $q_z=0.25$ this corresponds to an RF phase of 48° .

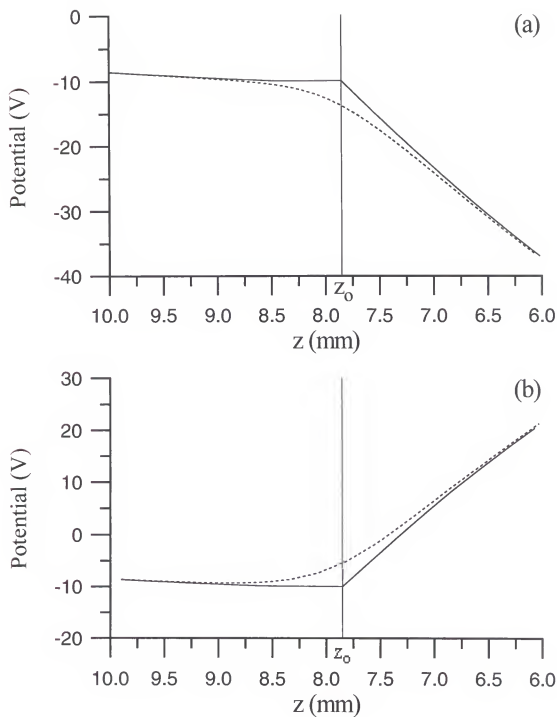


Figure 3-9 – Close up view of potential around entrance endcap under same conditions as in Figure 3-8.

are started at the inner plane of the endcap electrode will actually be started at a potential more negative than -10 V. Conversely, when the voltage on the ring electrode is initially positive (as in Figure 3-9b), ions which are started at the inner plane of the endcap electrode will be started at a potential more positive than -10 V. This effect increases as the voltage on the ring is increased, since the potential at the hole will be affected to a greater extent. This field penetration out the endcap hole will cause ions started with a constant kinetic energy at the inner plane of the endcap electrode to have different starting potential energies depending on the RF phase and q_z . These different starting potentials will result in ions which travel more slowly or rapidly than they otherwise would have because of the varying amounts of acceleration the ions experience as they move toward the center of the ion trap. The most straightforward way of dealing with this problem of field penetration out the endcap holes is to start ions sufficiently far outside the ion trap that the voltage on the ring does not affect the initial potential the ions experience.

Ions Injected from Outside Ion Trap

To determine what effect, if any, the RF trapping field had on ions which enter from outside the ion trap, ions were next started outside the ion trap and injected through the endcap hole. In these simulations, ions were started with a $z_{\text{init}}=19$ mm from the center of the ion trap to model ions traveling from the octopole toward the entrance endcap. The octopole, modeled as a cylindrical tube lens, was held at a potential of -6.5 V, the same as the experimental V_{O2} . In these simulations, ions were started with an E_0 equal to the experimental kinetic energy of ions in the second octopole, $E_0=3.5$ eV, so that they accelerated to 7 eV as they entered the ion trap which was held at a DC offset of -10 V. Ions were injected at different combinations of q_z and initial RF phase to map the

effect of these parameters on trapping efficiency. Since ions could not be started with very large angles from the z-axis, Θ , and still make it successfully through the endcap hole, ions were started with various x_{init} offsets with $y_{\text{init}}=0$ mm. By again starting ions at each RF phase and calculating the percentage of ions trapped over all RF phases, it was found that ions started at an x_{init} of 0.2 mm were trapped most efficiently (data not shown). An x_{init} of 0.2 mm was used for all subsequent simulations; to put this value into perspective, the inscribed radius of the octopole rods is 2.79 mm. As was shown in Chapter 2, a large portion of the initial axial kinetic energy of the ions was lost due to collisions in the first octopole. Off-axis, or radial, kinetic energy will be damped at the same time. Considering this collisional cooling, ions should have trajectories close to the center of the second octopole.

Simulations were again performed in which the q_z was varied from 0 to 0.9 in increments of 0.005 and the initial RF phase from 0° to 359° in 1° increments. At each combination, ten ions were injected with different random number generator seeds for the collision model simulating a pressure of 1.5 mtorr of helium. The initial RF phases are the RF phases at which the ions were started 19 mm from the center of the ion trap. Because of their flight times to the entrance endcap electrode, the ions actually arrived at the endcap at a different RF phase. With no voltage on the ring electrode, the transit time of m/z 100 ions was $3.965 \mu\text{s}$ to the inner plane of the entrance endcap ($z=z_0$). This translates to 1084.8° of RF phase or three full RF periods plus 4.8° . The voltage applied to the ring electrode causes ions to arrive earlier or later depending on the q_z and the RF phase at which they arrive. In addition, some combinations of q_z and RF phase cause ions not to enter the ion trap at all. This phenomenon will be discussed in depth later on in

this chapter. Since the effect of the ring electrode voltage on the arrival phase is complex, the simulation results will simply be plotted with respect to the average RF arrival phase defined as $(1084.8^\circ + \phi_{\text{RF}}) - (n \cdot 360^\circ)$. In other words, the approximate transit time to the ion trap is added to the starting phase of the ion. Then, an integer number of full RF periods ($n \cdot 360^\circ$) is subtracted to make the average RF arrival phase between -180° and 180° .

The results of the percentage of ions which are trapped at each q_z and average RF arrival phase are shown in Figure 3-10. The combinations which resulted in efficient trapping showed a bullet-shaped trend similar to that seen in Figure 3-7b for ions started at the plane of the entrance endcap; there are some important differences, however. First, the entire curve is shifted to higher phases, presumably due to field penetration out the endcap hole. Also, the bullet shape has been compressed vertically toward phases around 30° . Starting the ions at the inner plane of the entrance endcap ($z_{\text{init}} = z_0$) caused them to be started at varying potentials depending on the amount of voltage applied to the ring electrode. Starting ions at the inner plane of the entrance endcap with initial RF phases between -180° and 0° means the ions are started at potentials which are more negative than they would be without the hole (see Figure 3-9a). The ions, therefore, undergo less acceleration than they would have if started outside the ion trap, and behave as if they are lower kinetic energy ions. As will be seen in the next set of simulations for different kinetic energy ions, a lower kinetic energy translates to ions being trapped at lower RF phases. On the other hand, starting ions with RF phases between 0° and 180° means the ions are started at more positive potentials than they would be without the hole, and therefore undergo more acceleration (see Figure 3-9b). These higher kinetic energy ions

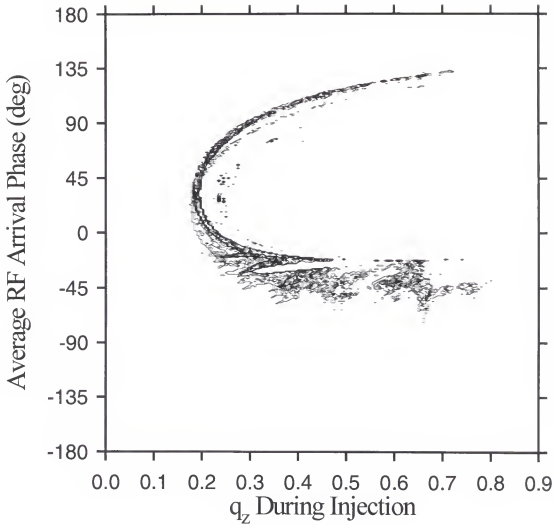


Figure 3-10 – Contour plot of the percentage of ions trapped as a function of RF phase and q_z for m/z 100 ions; simulated helium pressure of 1.5 mtorr. Holes in endcaps and ions started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV (ions accelerate to 7 eV as they enter ion trap).

are trapped at higher RF phases. This distortion in the RF phases over which ions are trapped in Figure 3-7b is eliminated by starting ions far enough outside the ion trap that field penetration out the endcap holes is insignificant (Figure 3-10).

Proposed Model for Trapping of Injected Ions

The simulations discussed up to this point used electrode geometry, helium pressure, and ion kinetic energies which closely approximate those in the LCQ. However, the question still remains as to why ions are trapped at particular q_z and RF phase combinations. Assuming a m/z 100 ion has a collision cross-section of $50 \text{ \AA}^2$, the mean free path is 41 mm with 1.5 mtorr of helium. The probability of a m/z 100 ion undergoing a collision before reaching the opposite endcap ($2z_0 = 15.7 \text{ mm}$) is only about 32%. In addition, the mass difference between the m/z 100 ion and a helium atom means that only a small fraction (7.4%) of the ion's kinetic energy is lost by the ion (see equation 3-3); thus, several collisions will be necessary to remove enough kinetic energy to trap the ion indefinitely. On this basis, it was speculated that ions may have trajectories at certain q_z and RF phase combinations in which the ions travel long distances in the ion trap, making possible enough collisions to remove significant kinetic energy from the ions.

In simulations, ions were injected without helium buffer gas and as expected, no ions were trapped indefinitely; indeed, 98.4% were lost within the first 20 μs . Examining the trajectories of thousands of injected ions led to the conclusion that in the absence of collisions, most ions go straight through the ion trap or turn right around and go back out the entrance endcap hole. However, there were a few q_z and RF phase combinations for

which the injected ions oscillated in the ion trap for up to 622 μs without the benefit of collisional damping. These ions were termed pseudo-stable ions since they underwent stable trajectories for hundreds of microseconds but were not stable indefinitely. It was reasoned that these pseudo-stable trajectories might provide enough time for a sufficient number of collisions to occur and damp the ion's kinetic energy to a point that the ion could be trapped indefinitely. This is an extension of an idea by Chun-Sing O and Hans Schuessler⁵³ whose simulations indicated that injected ions could be stable for long enough, without the benefit of collisions, to perform spectroscopic measurements of the ions.

To test this hypothesis, simulations were performed with the q_z during injection varied from 0 to 0.9 in increments of 0.005 and the initial RF phase varied from 0° to 359° in 1° increments. At each combination, a single ion was started outside the ion trap at $z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, and $y_{\text{init}}=0$ mm with 3.5 eV of kinetic energy (the same conditions as for the data shown in Figure 3-10) with the collision model disabled. Instead of recording whether the ions were trapped for >400 μs (since none of them were), the time they remained in the ion trap as well as the total distance they traveled before being lost to an electrode or endcap hole was recorded. These data are plotted in a contour plot in Figure 3-11, where the z-axis is the total distance traveled inside the ion trap. The white portion of the contour plot corresponds to ions which traveled less than 14 mm within the ion trap before striking an electrode or exiting through an endcap hole. These are mainly ions which turned around shortly after entering the ion trap. The lightest gray portion (14-25 mm traveled) of the plot shows ions which went straight through the ion trap and struck the exit endcap or went through the exit endcap hole. At

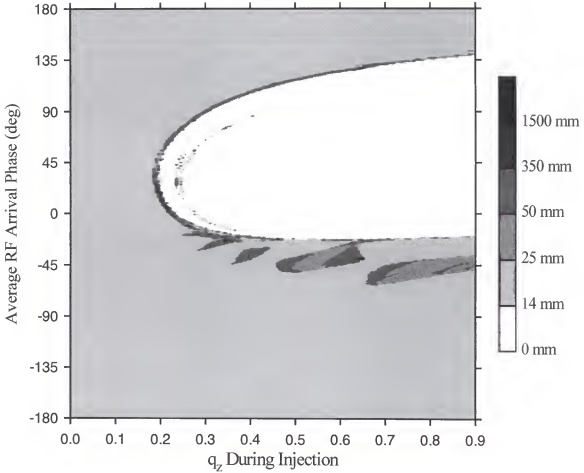


Figure 3-11 – Contour plot of the distance traveled by m/z 100 ions in the ion trap before being lost to an electrode or endcap hole with no helium buffer gas as a function of RF phase and q_z . Ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV (ions accelerate to 7 eV as they enter ion trap). The q_z and RF phase combinations which resulted in “naturally” pseudo-stable trajectories are the same ones for which ions were trapped indefinitely when collisions with helium buffer gas were simulated (see Figure 3-10).

some combinations of q_z and RF phase, the ions turned around just before striking the exit endcap and made multiple passes through the ion trap (25-1500 mm). At even fewer combinations of q_z and RF phase, the ions oscillated for even longer distances without the benefit of collisional damping (>1500 mm). Overall, the same bullet-shaped trend was observed for the longest distances traveled as was seen for the highest trapping efficiency in Figure 3-10. The q_z and RF phase combinations for which ions “naturally” oscillated for extended periods of time (and therefore traveled large distances without collisional damping) were the same q_z and RF phase combinations for which ions were trapped indefinitely when buffer gas was added. In other words, these ions were “naturally” pseudo-stable because of the particular q_z and RF phase combination used. The ions were not stable indefinitely, but were stable long enough for sufficient collisions to occur to collisionally damp the ions and allow them to be trapped indefinitely.

The relationship between pseudo-stable distance traveled and the trapping of ions with helium buffer gas can be compared more closely by studying vertical slices through Figure 3-10 and Figure 3-11. Ions of m/z 100 were injected as before from outside the ion trap with $E_0=3.5$ eV and $z_{\text{init}}=19$ mm from the center of the ion trap and $x_{\text{init}}=0.2$ mm and $y_{\text{init}}=0$ mm. Holding the q_z constant at 0.3, the initial RF phase was varied between 0° and 359° in 0.2° increments. The distance traveled is shown on a logarithmic scale in Figure 3-12b. The left and right sides of the curve (distances traveled around 15 mm) correspond to ions which go straight through the ion trap and are analogous to the lightest gray area in Figure 3-11. RF phases with short distances traveled (<5 mm) correspond to ions which did not penetrate very deeply into the ion trap, as in the white area in Figure 3-11. Between the RF phases where ions go straight through and those where the ions turn

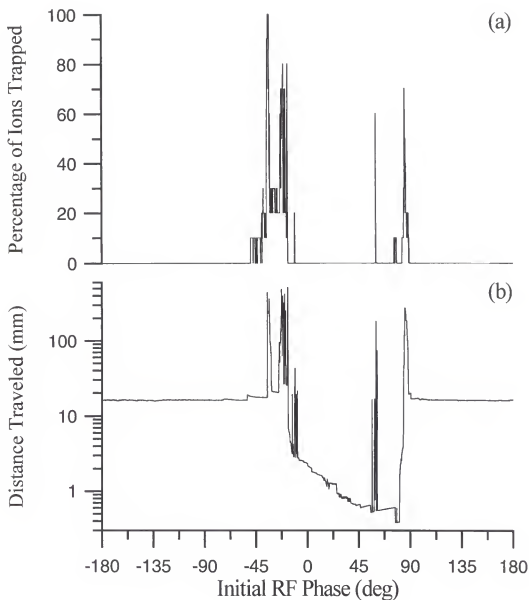


Figure 3-12 – Comparison of the percentage of m/z 100 ions trapped at 1.5 mtorr of helium and the distance traveled in the ion trap before being lost to an electrode or endcap hole with no helium buffer gas. Ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, and $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV (ions accelerate to 7 eV as they enter ion trap); $q_z=0.3$. (a) Percentage of ions trapped at helium pressure of 1.5 mtorr. (b) Vertical slice from Figure 3-11 showing distance traveled (on a logarithmic scale) as a function of initial RF phase; distances vary from 0.7 mm to 500 mm.

right around are RF phases where ions travel distances between 15 mm and 500 mm before being lost to an electrode or through an endcap hole. The percentage of ions trapped for $>400 \mu\text{s}$ at a helium pressure of 1.5 mtorr is shown in Figure 3-12a. There is a strong correlation between those RF phases which resulted in “naturally” pseudo-stable trajectories and those for which ions are trapped when helium is added. Ions are only trapped at those RF phases for which ion trajectories are pseudo-stable for the longest distances. This relationship will be explored in more detail in the beginning of Chapter 4.

Ion Injection Simulations of m/z 1522 Ions

Effect of Endcap Holes on Ion Injection

With the insight gained from simulations of m/z 100 ions, a higher m/z ion was simulated to investigate any differences. First, the effect of endcap holes was studied. Ions were started at the inner plane of the entrance endcap electrode ($z_{\text{init}}=z_0=7.85 \text{ mm}$, $x_{\text{init}}=0 \text{ mm}$, and $y_{\text{init}}=0 \text{ mm}$). From the stopping potential measurements for the commercial skimmer shown in Chapter 2, the average kinetic energy of m/z 1522 ions entering the ion trap was 7.5 eV. For the following simulations, an initial kinetic energy, E_0 , of 7.5 eV was used. The q_z was varied from 0 to 0.3 in increments of 0.005, while initial RF phase was varied from 0° to 359° in 1° increments. At each combination, ten ions were injected with different random number generator seeds for the collision model simulating a pressure of 1.5 mtorr of helium; a collision cross-section of $300 \text{ \AA}^2$ was used. The data were plotted in a series of contour plots where the z -axis is the percentage of the population of ten ions which were trapped. The results for the electrode grid without endcap holes are shown in Figure 3-13a, while the results with endcap holes are

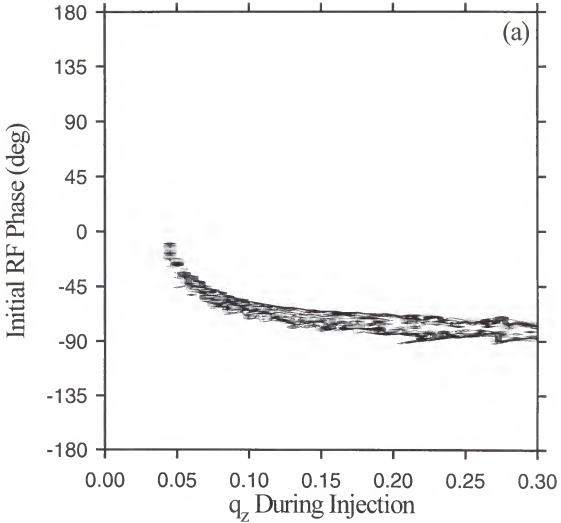


Figure 3-13 – Contour plots of the percentage of ions trapped as a function of RF phase and q_z for m/z 1522 ions; simulated helium pressure of 1.5 mtorr. (a) No holes in endcaps and ions started at the inner plane of the entrance endcap ($z_{\text{init}}=7.85$ mm, $x_{\text{init}}=0$ mm, $y_{\text{init}}=0$ mm, and $\Theta=10^\circ$) with $E_0=7.5$ eV. (b) Holes in endcaps and ions started under the same conditions as in (a). Each of these simulations took over 4 days to complete.

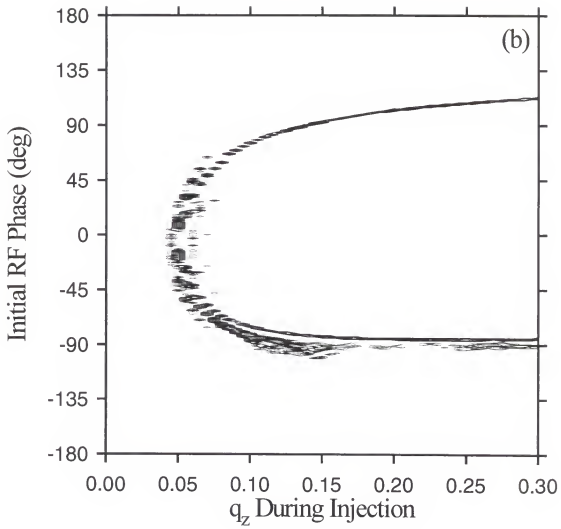


Figure 3-13 – continued.

shown in Figure 3-13b. Just as was observed for m/z 100, without endcap holes only a single range of RF phases resulted in favorable trapping. With endcap holes, another bullet-shaped distribution resulted. The main difference in the results compared to m/z 100 ions is that m/z 1522 ions were trapped at lower q_z values; this is consistent with experimental observations in Chapter 2. In addition, the bullet-shaped distribution for m/z 1522 had a flatter front meaning ions were trapped over a wider range of RF phases at low q_z values.

Ions Injected from Outside Ion Trap

The next step was to inject ions from outside and investigate the effect of the field distortion near the holes. Ions were started outside the ion trap at $z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, and $y_{\text{init}}=0$ mm with 4.0 eV of kinetic energy (ions accelerate to 7.5 eV as they enter the ion trap). The q_z during injection was varied from 0 to 0.3 in increments of 0.005 while initial RF phase was varied from 0° to 359° in 1° increments. The percentage of ions trapped with 1.5 mtorr of helium buffer gas is shown in Figure 3-14. Instead of the anticipated bullet-shaped curve, an s-shaped curve was obtained. When ions were started at the endcap boundary, the simulations predicted efficient trapping out to $q_z \approx 0.8$ (data not shown). With ions started outside the ion trap, no ions are seen trapped above a $q_z \approx 0.2$, presumably because of the distorted field around the endcap holes.

To determine what effect the holes were having on ions, hundreds of ion trajectories were studied. These results can be summed up in three representative trajectories shown in Figure 3-15. Here, the potentials three different ions experience as they approach the ion trap are shown as a function of time. The right edge of these plots is the time that the ions arrive at the inner plane of the entrance endcap ($z=z_0$) with no RF

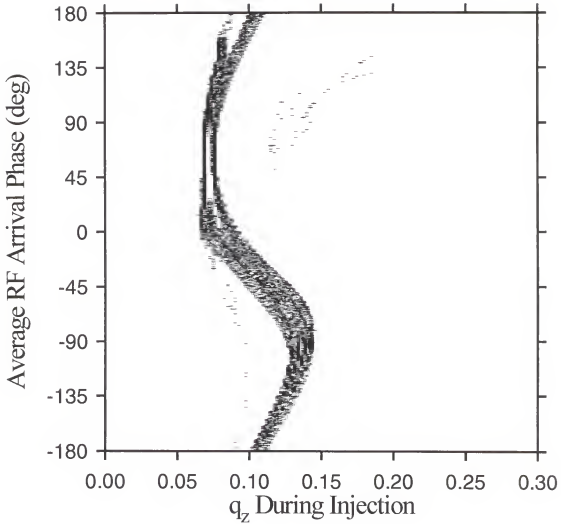


Figure 3-14 – Contour plot of the percentage of ions trapped as a function of RF phase and q_z for m/z 1522 ions; simulated helium pressure of 1.5 mtorr. Holes in endcaps and ions started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=4.0$ eV (ions accelerate to 7.5 eV as they enter ion trap).

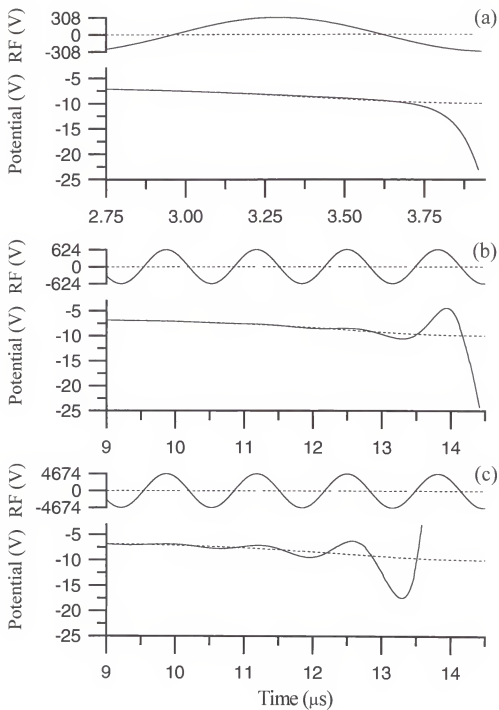


Figure 3-15 – Plots of the RF voltage and the potential ions experience as a function of time. These three ions approach the ion trap from outside; the right edge of the graph is the time the ions arrive (or would have arrived) at the inner plane of the entrance endcap ($z=z_0$). The dotted line is the result for no RF voltage applied to the ring electrode. (a) m/z 100 ion injected at $q_z=0.6$. (b) m/z 1522 ion injected at $q_z=0.08$. (c) m/z 1522 ion injected at $q_z=0.6$; ion is repelled before it reaches the ion trap.

voltage applied to the ring electrode. All three of these ions were started under conditions such that they arrived at the entrance endcap at an RF phase of -90° in the absence of an RF voltage on the ring (shown as a dotted line). In Figure 3-15a, a m/z 100 ion was injected at a q_z of 0.6. With the RF voltage applied to the ring electrode (308 V_p), the potential outside the endcap was affected and the ion actually arrived at the endcap slightly earlier. The reason for this can be seen by returning to Figure 3-9 where the RF field from the ring electrode was seen to penetrate out the endcap hole.

This effect of the RF field on the approaching ion is even more dramatic for a m/z 1522 ion injected at a $q_z=0.08$, as shown in Figure 3-15b. Here, the RF field which penetrates out the endcap was even stronger because the RF voltage on the ring electrode was approximately twice as high (624 V_p) as in Figure 3-15a. More importantly, the m/z 1522 ion was moving slower than the m/z 100 ion; therefore, the m/z 1522 ion interacted with more RF periods than the m/z 100 ion. Although the m/z 1522 ion should have arrived at the ion trap at an RF phase of -90° , it interacted strongly with a positive phase of the RF voltage when the ion was approximately 0.55 mm outside the ion trap. This interaction presented the ion with a potential hill which, fortunately, the ion was able to climb. The only side effect was the ion arrived at the endcap slightly later than it would have if it were not for this RF field penetration. This potential hill got larger when the RF voltage on the ring electrode was increased (higher q_z). Figure 3-15c shows the case for a q_z of 0.6, where the ion was affected by the RF voltage on the ring electrode as far as 4.5 mm from the entrance endcap. This interaction was so strong that an insurmountable potential hill repelled the ion when it was 0.6 mm from the inner boundary of the endcap. Although ions can be trapped at high q_z (as shown in Figure 3-13b), this RF field

penetration prevents them from ever entering the ion trap. A similar effect was reported in the literature where the authors mentioned that some of their computer simulations showed that ions which arrived at the wrong RF phases could be forced back into the endcap hole and therefore never get into the ion trap.⁷ Although the authors were correct, they did not appreciate that ions could actually be repelled long before they even reach the ion trap. Or, even if the RF field penetration was not strong enough to repel the ions, it could cause the ions to arrive earlier or later than they otherwise would have. These effects cause the bullet-shaped curve (Figure 3-13b) to open up to an s-shaped curve (Figure 3-14).

The effect of the RF field penetration can be seen more clearly by simulating various ions with m/z values between 100 and 1522. To save simulation time, the distance traveled inside the ion trap was recorded with no collisions rather than the percentage of ions trapped with collisions. As demonstrated previously, longer natural distances translate to a higher percentage of ions trapped when buffer gas is introduced. Simulations were run for ions started outside the ion trap at $z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, and $y_{\text{init}}=0$ mm. The q_z was varied from 0 to 0.9 in increments of 0.02 while the initial RF phase was varied from 0° to 358° in 2° increments. Ions of m/z 100, 195.1, 524.3, 750, and 1022 were started with $E_0=3.5$ eV (ions enter the ion trap with 7 eV); ions of m/z 1522 were started with $E_0=4.0$ eV (ions enter the ion trap with 7.5 eV). The six contour plots of the distance traveled inside the ion trap are shown in Figure 3-16. With increasing m/z , there is a continuous evolution of the bullet-shape of m/z 100 opening up. This appears to occur as the RF voltage on the ring electrode increases and ions enter the ion trap more slowly at higher m/z .

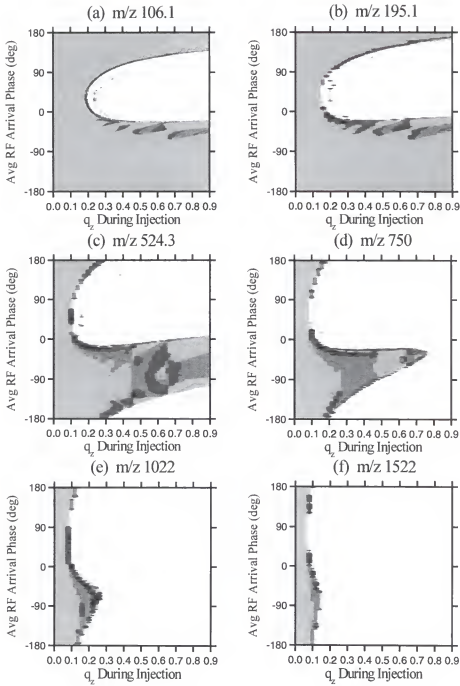


Figure 3-16 – Contour plots of the distance traveled inside the ion trap in the absence of collisions by different m/z ions injected from outside. (a) m/z 106.1, (b) m/z 195.1, (c) m/z 524.3, (d) m/z 750, (e) m/z 1022, and (f) m/z 1522. z-axis scale is the same as in Figure 3-11.

Comparison of Ion Injection Experiments to Computer Simulations

SIMION computer simulations have provided quite a bit of insight into how injected ions are trapped. However, the SIMION model has also raised several questions about the effect of endcap holes and RF field penetration. Although these effects make sense, they have not been reported in the literature and cannot be easily measured experimentally. What has been measured experimentally is the relative trapping efficiency as a function of the LMCO during injection. The ability of the simulations to predict these experimental observations would lend some validity to the model and many of its other predictions.

Since electrospray is a continuous ionization source, the percentage of the ions successfully trapped at each q_z can be calculated by summing the number of ions trapped over all initial RF phases and dividing by the total number of ions injected at that q_z . The percentage of m/z 100 ions trapped at each q_z in Figure 3-10 was calculated and is plotted in Figure 3-17. Also, the experimental variation of m/z 106.1 is shown for comparison. Overall, the results do not agree very strongly; the simulated data show a sharp spike of high injection efficiency at the left edge near $q_z=0.2$ and a gradual drop in efficiency at higher q_z . In contrast, the experimental data show a sloping left edge between $q_z=0.15$ and 0.2 and a broader optimum. In the simulation, there was an interesting increase in trapping efficiency around a q_z of 0.65; a similar increase in trapping efficiency has been previously reported.⁷⁹ Although the exact cause of the increase is unknown, it is suspected to result from an octopolar non-linear resonance.

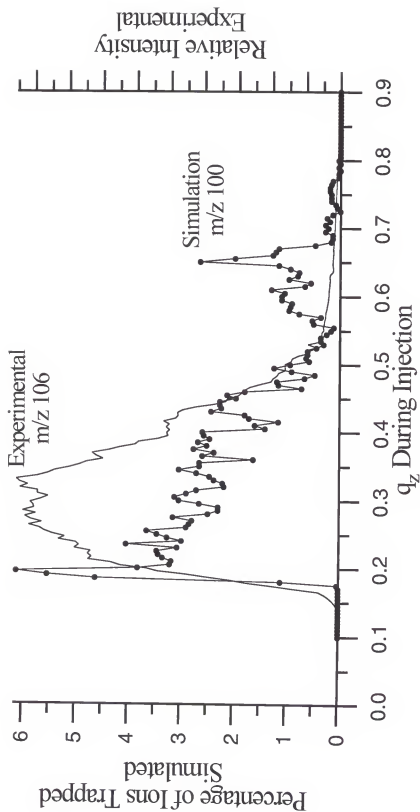


Figure 3-17 – Comparison of simulation of m/z 100 and experimental ion injection data for m/z 106.1. Simulated data show the percentage of ions trapped at each q_z (out of 3,600) over all RF phases for a single kinetic energy of 7 eV.

One reason for the inconsistency between simulation and experiment was the simulation used ions of only a single kinetic energy, 7 eV. This kinetic energy was chosen because it was the center of the energy distribution as measured by experimental stopping potentials for m/z 106.1. However, the derivative of the stopping potential data also provided the kinetic energy distribution of the ion beam. The kinetic energy distribution was centered at 7 eV; however, it had a full-width at half of maximum (FWHM) kinetic energy spread of approximately 2.5 eV (see Figure 2-6). This relatively broad kinetic energy distribution was caused by collisions in the first octopole⁵⁵ which contained approximately 2 mtorr of nitrogen. To determine the effect of kinetic energy on ion injection, simulations such as those summarized in Figure 3-10 were repeated for ions with initial kinetic energies of 1.5, 2.5, 4.5, and 5.5 eV to simulate ions entering the ion trap with 5, 6, 8, and 9 eV kinetic energies. From these data, the left edge of the bullet-shaped curve in Figure 3-10 was found to shift to higher q_z at higher injection kinetic energies. This is consistent with the experimental observation that higher kinetic energy ions are more efficiently trapped at higher q_z values.²⁹ Also, as the kinetic energy was increased, the bullet-shaped curve became narrower in phase, resulting in a shift in the advantageous RF phases toward the center of the bullet.

Since ions of different initial kinetic energies travel at different velocities, the transit time to the entrance endcap is different. To allow all five kinetic energy simulation plots to be shown together, the initial RF phases were converted to the average RF arrival phase, as in Figure 3-10. Next, the number of ions trapped at each kinetic energy was scaled based on the percentage of ions in the experimental ion beam with that kinetic energy (see Figure 2-6). A contour plot summarizing all five kinetic energies

between 5 and 9 eV is shown in Figure 3-18. The effect of the weighted summing of a range of kinetic energies is to broaden the range of q_z values and RF phases over which ions are trapped, as can be observed by comparing Figure 3-10 and Figure 3-18. The percentage of ions trapped over all RF phases was then calculated for each q_z as in Figure 3-17. This new simulated profile for m/z 100 is shown in Figure 3-19 along with the experimental data for m/z 106.1.

Overall, the agreement between the simulation and experimental data is quite good at q_z values below 0.55. The weighted summing of multiple kinetic energies has the effect of broadening the range of q_z values over which ions are trapped so that a broader optimum results like that seen experimentally. At q_z values above 0.55, a possible explanation for the discrepancy between the experimental and simulated data shown in Figure 3-19 would be ion fragmentation. It has been observed experimentally that the ion signal of injected ions drops off at high q_z during injection, primarily because the injected ions fragment.^{29,43,80} At high q_z values for injection, fragment ions of m/z 106.1 were observed in the spectra for the data shown in Figure 3-19. According to pseudopotential well theory, the average kinetic energy of an ion is proportional to q_z^2 ; therefore, at higher q_z values ions undergo more energetic collisions.¹⁴ Also, at higher kinetic energy the ions are moving faster and travel more distance per unit time; therefore, they undergo more collisions per unit time. Since the hard-sphere collision model in the simulation does not take into account internal energy deposition or fragmentation, the simulation may predict trapping at q_z values for which experimental ions fragment. It would be interesting to incorporate fragmentation into future computer simulation studies.

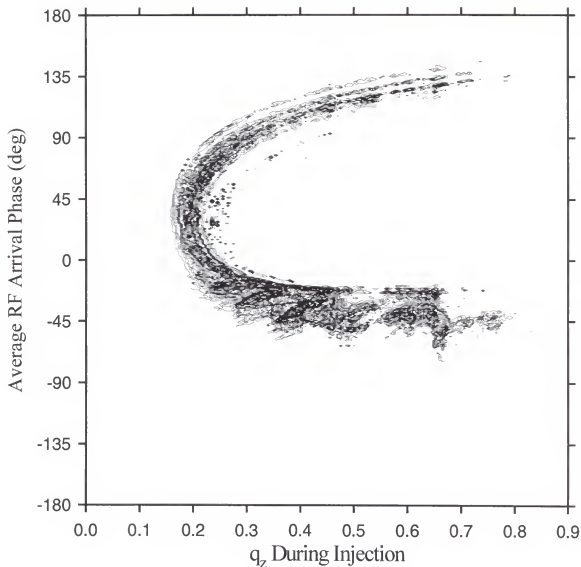


Figure 3-18 – Contour plot of the percentage of ions trapped as a function of average RF arrival phase and q_z , compiling simulations of m/z 100 ions injected at 5, 6, 7, 8, and 9 eV. The simulations of multiple kinetic energies were weight summed according to the percentage of each kinetic energy found in the experimental ion beam for m/z 106.1. Lower kinetic energy ions are trapped at lower q_z values. Initial RF phase was converted to average RF arrival phase to allow all five simulations to be compared on the same plot. Ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$). Simulated helium pressure of 1.5 mtorr.

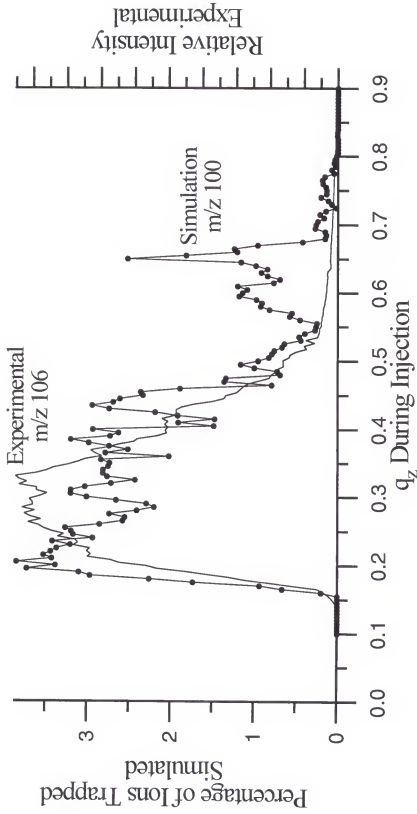


Figure 3-19 – Comparison of simulation of m/z 100 and experimental ion injection data for m/z 106.1. Simulated data show the percentage of ions trapped at each q_z (out of 18,000) over all RF phases weighted for an experimentally determined range of kinetic energies (5 - 9 eV).

In addition to modeling the ion injection trends seen experimentally, the simulation also provides absolute percentages of ions trapped at each q_z , which is quite challenging to measure experimentally. The maximum percentage of m/z 100 ions trapped was found to be around 3% for q_z values between 0.2 and 0.4. This trapping efficiency is consistent with what has been measured experimentally.^{40,43} It should be noted that the data shown in Figure 3-18 and Figure 3-19 consisted of simulations of $(3,600 \text{ ions/energy}/q_z) \times (5 \text{ energies})$ or 18,000 total ions at each q_z . With the 181 q_z values simulated, these plots comprised 3,258,000 ions and required 28 days to simulate.

This same type of analysis was performed for m/z 1522. From experimental stopping potential measurements in Chapter 2, m/z 1522 ions were found to have an average kinetic energy of 7.5 eV and a 2.5 eV FWHM distribution of kinetic energies (see Figure 2-6). Additional simulations were run with initial kinetic energies of 2, 3, 5, and 6 eV to simulate ions entering the ion trap with 5.5, 6.5, 8.5, and 9.5 eV. The percentage of ions trapped at each kinetic energy was weighted based on the experimental stopping potential distribution (Figure 2-6); the resulting contour plot is shown in Figure 3-20. The left edge of the s-shaped curve was found to shift to higher q_z at higher injection kinetic energies. Also, as the kinetic energy was increased, the s-shaped curve flattened out, narrowing the range of efficient q_z values. At the same time, ions were trapped over a wider range of RF phases than for the higher velocity, lower m/z 100 ion.

The percentage of the ions successfully trapped at each q_z was calculated by summing the number of ions trapped over all initial RF phases and dividing by the total number of ions injected at that q_z . The percentage of m/z 1522 ions trapped is plotted as

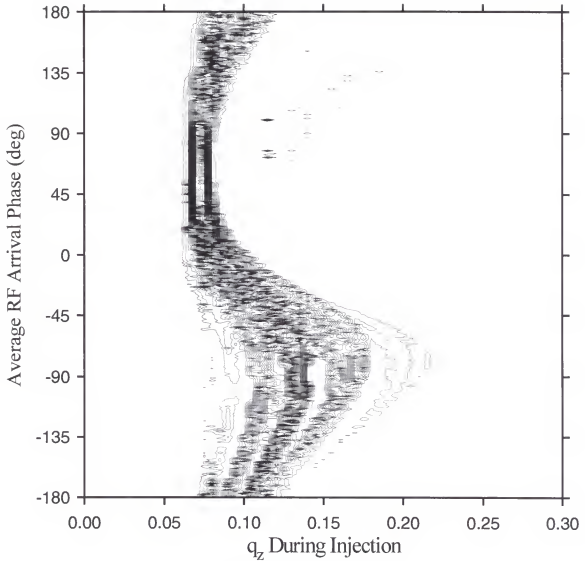


Figure 3-20 – Contour plot of the percentage of ions trapped as a function of average RF arrival phase and q_z compiling simulations of m/z 1522 ions injected at 5.5, 6.5, 7.5, 8.5, and 9.5 eV. The simulations of multiple kinetic energies were weight summed according to the percentage of each kinetic energy found in the experimental ion beam for m/z 1522. Lower kinetic energy ions are trapped at lower q_z values. Initial RF phase was converted to average RF arrival phase to allow all five simulations to be compared on the same plot. Ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$). Simulated helium pressure of 1.5 mtorr.

a function of q_z during injection in Figure 3-21 and shown in comparison to the experimental variation of m/z 1522. The simulations do not predict as wide a range of q_z values for efficient trapping as observed experimentally. This and the humps observed in the tail of the simulation data may be a result of the discrete kinetic energies used as well as the simulation of only a single initial position. More simulations may improve the agreement between simulation and experiment; however, the data shown already represent the combined simulations of 1,098,000 ions and took 20 days to simulate. Despite these differences, it is important to note that the m/z 1522 ions were trapped over a narrower range of q_z values and centered at a lower q_z than the m/z 100 ions. The optimum q_z for trapping was ≈ 0.3 for m/z 100 and ≈ 0.075 for m/z 1522. This corresponds to an RF voltage of 154 V_p for m/z 100 and 584 V_p for m/z 1522. The slower moving m/z 1522 ion is affected to a greater extent than the m/z 100 ion by RF field penetration as it approaches because of the larger RF voltages on the ring electrode, as shown in Figure 3-15. This RF field penetration is beneficial in this case because a higher percentage of ions are trapped than for m/z 100; in fact, the trapping efficiency was 22.6% for m/z 1522 (Figure 3-21) versus 3.9% for m/z 100 (Figure 3-19). This observation is interesting and will be examined in more detail in the next chapter.

Although the agreement between the simulated and experimental data was quite good, the question remains as to how important it is in simulations to start ions outside the ion trap. Recall that the RF fringe field dramatically changed the shape of the RF phase and q_z contour plot for ions started outside the ion trap (compare Figure 3-13b to Figure 3-14). As a simple test, additional simulations were run starting m/z 1522 ions at the endcap boundary (with endcap holes) with initial kinetic energies of 6, 7, 8, 9, 10, and

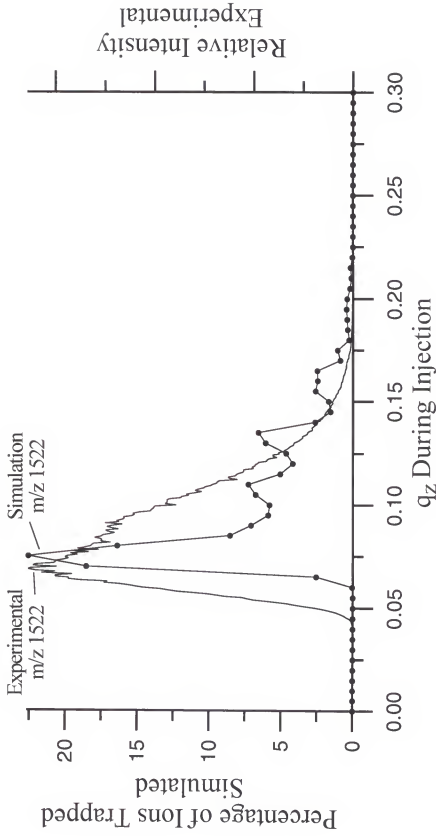


Figure 3-21 – Comparison of simulation of m/z 1522 and experimental ion injection data for m/z 1522. Simulated data show the percentage of ions trapped at each q_z (out of 18,000) over all RF phases for an experimentally determined range of kinetic energies (5.5 - 9.5 eV).

11 eV. The percentage of ions trapped at each kinetic energy was weighted based on the experimental stopping potential distribution just as was done for Figure 3-21. The percentage of ions trapped at each q_z is plotted in Figure 3-22. Clearly, the agreement between simulation and experiment is not as good as in Figure 3-21 when ions were started outside the ion trap and forced to cross the RF fringe field. The optimum q_z predicted when ions were started at the endcap boundary is not as accurate as for starting ions outside (as expected from a comparison of Figure 3-13b and Figure 3-14). However, the main discrepancy is the simulations starting ions at the endcap predicted trapping well beyond a q_z of 0.2, where experimentally no ions were observed. Although it is tempting to explain this with the same ion fragmentation at high q_z argument used above, no fragmentation was observed experimentally. The hypothesis is that although ions can be trapped at these higher q_z values, the RF fringe field prevents ions from entering the ion trap in the first place. RF field penetration out of the endcap hole suggests that simulation programs which only model the field within the ion trap (forcing ions to be started at the endcap boundary) are not adequate for simulating ion injection.

Implications of SIMION Computer Model

In this chapter and the previous one, ion injection into a quadrupole ion trap mass spectrometer was studied by both simulation and experiment. SIMION was chosen because it allowed the actual electrode geometry including endcap holes to be simulated. The endcap holes weaken the RF trapping field in the region near the holes; this distortion of the field is important when ions have large axial trajectories as they do in ion injection. All previous simulations of ion injection have predicted a single, narrow range

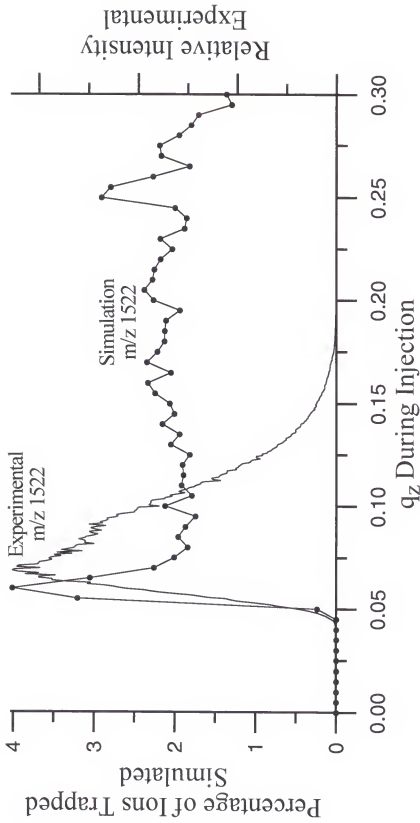


Figure 3-22 – Comparison of simulation of m/z 1522 and experimental ion injection data for m/z 1522. Simulated data are for ions started at the inner plane of the entrance endcap rather than outside the ion trap as in Figure 3-21. The percentage of ions trapped at each q_z over all RF phases is shown for an experimentally determined range of kinetic energies (6 - 11 eV).

of RF phases when the voltage on the ring electrode is initially negative for which injected ions are successfully trapped. However, the inclusion of the endcap holes created a weakened RF trapping field near the holes which allowed ions to be trapped over a second narrow range of RF phases when the ring is initially positive.

Simulations performed with the SIMION ion injection model agreed well with experimental ion injection data of electrosprayed ions. The simulations started ions sufficiently far outside the ion trap to make field penetration out of the endcap hole from the voltage applied to the ring electrode insignificant. Even the relatively fast moving m/z 100 ions were found to interact with the RF field which penetrates out the endcap hole. This field penetration affected the phase at which the ions entered the ion trap by slowing down and speeding up the ions as they approached the entrance endcap.

A model for the process by which injected ions are trapped was developed using the SIMION simulations. Injected ions can be trapped even with the modest helium buffer gas pressures commonly used (≈ 1 mtorr) because ions naturally oscillate for long times (and therefore distances) at certain q_z and initial RF phases. This allows enough collisions to occur to damp the ions' excess kinetic energy. However, the small range of favorable RF phases and the inefficiency of collisional damping demands further study to maximize the number of ions which are trapped. Methods of improving the trapping efficiency of injected ions are presented in Chapter 4.

CHAPTER 4

METHODS OF IMPROVING TRAPPING EFFICIENCY FROM A CONTINUOUS IONIZATION SOURCE

Introduction

Continuous ionization sources present an especially challenging situation for efficient ion injection and trapping because ions must be accumulated over time; therefore, any method of improving trapping efficiency cannot disturb ions which are already in the ion trap. This chapter begins with a brief introduction to trapping ions from continuous sources. Then, three different methods of improving trapping efficiency which are compatible with continuous ionization sources will be presented. The first method uses higher pressures of helium buffer gas (or alternately, a heavier buffer gas) and has been shown previously to increase trapping efficiency.^{31,60,81,82} The shortcomings of this method including the time required to pump out the added buffer gas before mass analysis will be addressed.

Two alternative novel techniques of increasing trapping efficiency will be described. The first is based on simulation data presented in Chapter 3 that suggest ions which enter the ion trap with low velocities are trapped with higher efficiencies. These low velocity ions are trapped at low q_z values where less RF phase-dependency exists. As a result, a larger range of RF phases result in efficient trapping. Although this method has not been attempted experimentally, simulation results will be presented along with

some potential challenges including inefficient transmission of low velocity ion beams. The second novel method uses periodic time-varying voltages to vary the kinetic energy and time at which ions arrive at the ion trap with respect to RF phase. The development of this method of phase-sympathetic injection will be described and three-fold experimental increases in trapping efficiency will be shown as well as the potential for even larger improvements.

Improving Trapping Efficiency from Continuous Ionization Sources

The trapping of injected ions requires two separate steps. First, ions must arrive at an appropriate RF phase for their kinetic energy so that they can enter the ion trap. Second, some process of removing excess kinetic energy is needed to prevent ions from leaving the ion trap. It has been well established that there is only a small range of RF phases over which externally formed ions can be successfully trapped.^{53,61} Computer simulations of the LCQ in Chapter 3 predicted that m/z 100 ions are only trapped over less than 20° of RF phases at a helium buffer gas pressure of 1.5 mtorr.

When dealing with ionization sources which produce a single pulse of ions, there are several techniques available for improving trapping efficiency. If the temporal spread of the ion pulse is on the order of the phase acceptance of the ion trap, simply synchronizing the ion beam arrival with the RF phase window will produce efficient trapping. For m/z 100 this would correspond to a temporal spread of $(20^\circ/360^\circ) \times (1/760000 \text{ Hz}) = 0.07 \text{ } \mu\text{s}$. If the ion beam is temporally wider, techniques such as dynamic trapping,^{5,33-37} RF damping voltages,⁷ or DC pulses^{41,83} have been used (see Chapter 1). However, all of these techniques disturb ions which may already be in the ion

trap, preventing ions from being accumulated over more than a single pulse. Therefore entirely different techniques are necessary for trapping ions from continuous ionization sources.

Since the ion beam from a continuous source contains a steady stream of ions, any technique used to trap ions must have a high duty cycle and cannot interfere with ions which are already in the ion trap. This leaves only two possible options, increasing the phase acceptance window of the ion trap or continuously manipulating the ion beam to make it more compatible with the phase acceptance of the ion trap. These two options will be discussed in turn.

Increasing the Phase Acceptance Window of the Ion Trap

By increasing the phase acceptance window of the ion trap, a higher percentage of a continuous ion beam can be trapped; this in effect increases the duty cycle. The concept of pseudo-stable trajectories presented in Chapter 3 implies that ions injected at certain RF phase/ q_z combinations will be “stable” in the ion trap for relatively long periods of time even without buffer gas. These ions can only be indefinitely trapped if excess kinetic energy is removed in a timely manner. By increasing the helium buffer gas pressure, ions will lose kinetic energy more rapidly. This should allow RF phase/ q_z combinations with shorter natural pseudo-stable distances to result in efficient trapping. This should translate to a larger range of RF phases over which ions can be trapped. The use of higher helium buffer gas pressures for improved ion injection efficiency has been showed experimentally by several groups.^{31,60,81} Not only is a higher buffer gas pressure effective in improving trapping efficiency, but so is the use of heavier gases such as argon

and xenon.⁸² These heavier gases remove more kinetic energy per collision because of their higher mass (see equation 2-4).

Ion Injection Simulations at Higher Buffer Gas Pressures

To understand how an increased helium pressure can improve the trapping efficiency of injected ions, a series of computer simulations were run. Ion injection simulations of ions started at the endcap boundary using higher helium pressures have been shown in the literature.^{41,60} In this work, ions of m/z 100 were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV (ions accelerate to 7 eV as they enter the ion trap). Holding the q_z constant at 0.3, the initial RF phase was varied between 0° and 359.8° in 0.2° increments. The pseudo-stable distance traveled by an injected ion before being lost to an endcap hole or electrode, in the absence of helium buffer gas, is shown in Figure 4-1a. This curve is the same as the one shown in Figure 3-12b. At most of the RF phases, ions go straight through the ion trap or turn around without penetrating very deeply. However, at the RF phases between where ions go straight through and ions turn right around are RF phases where ions travel distances between 15 mm and 500 mm before being lost to an electrode or endcap hole. The percentage of ions trapped for >400 μs (and presumably indefinitely) at different initial RF phases is shown for different helium pressures in Figure 4-1b to Figure 4-1e. There is a strong correlation between those RF phases which result in “naturally” pseudo-stable trajectories and those for which ions are trapped when helium is added. At low pressures, ions are only trapped at those RF phases for which ions are pseudo-stable for the longest distances. As the pressure is increased, shorter distances are necessary to undergo enough collisions to damp the ion’s excess kinetic energy. The result of higher pressures is to

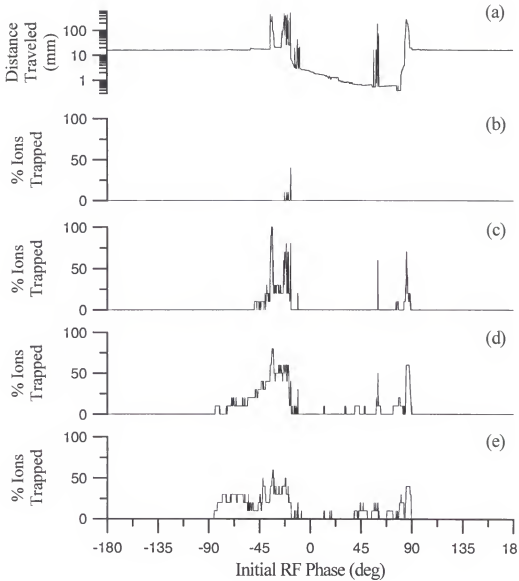


Figure 4-1 – Comparison of distance traveled by m/z 100 ions in the ion trap before being lost to an electrode or endcap hole with no helium buffer gas and the percentage of ions trapped at various simulated helium pressures. (a) Distance traveled (on a logarithmic scale) as a function of initial RF phase; distances vary from 0.7 mm to 500 mm. (b-e) Percentage of ions trapped at various helium pressures. (b) 0.1 mtorr helium. (c) 1.5 mtorr helium. (d) 4.5 mtorr helium. (e) 7.5 mtorr helium.

trap ions over a larger range of RF phases. This larger phase acceptance translates to higher overall trapping efficiency when a continuous ionization source is used. By integrating the total number of ions trapped over all RF phases, the percentage of ions trapped at each helium pressure can be determined. For helium pressures of 0.1, 1.5, 4.5, and 7.5 mtorr, the trapping efficiencies were 0.061%, 2.9%, 6.3%, and 6.4% respectively. Pressures higher than 7.5 mtorr were not attempted because collisions were assumed to occur at all spatial positions in the simulation. At these high pressures, ions would lose a significant amount of their kinetic energy before even reaching the ion trap.

Problems with Using Increased Buffer Gas Pressure

Although the trapping efficiency may be improved through the use of higher pressures or heavy gases, other portions of the scan function may be adversely affected.^{40,82} An alternative is to use a pulsed valve to allow a higher pressure of buffer gas to be used during ion injection; this extra buffer gas is then pumped away before mass analysis.⁶⁰ One problem with the commonly used pulsed valves is the pressure profile obtained from them. A typical pulsed valve consists of a solenoid driven poppet followed by a small orifice (≈ 0.006 in diameter). When the solenoid is opened, the pressure will rise very quickly within the analyzer region, provided the amount of connective tubing which delivers the helium into the vacuum chamber is minimized. This is most easily accomplished by mounting the pulsed valve inside the vacuum chamber near the ion trap.⁸⁴ Then, when the solenoid is closed, the pressure in the analyzer will decay slowly as the gas in the dead volume between the poppet and the orifice bleeds out. To eliminate this long decay time, the dead volume must be minimized; however, there is a finite

mechanical limitation to how small this dead volume can be made. Other pulsed valve configurations have been devised to help create a more square pressure profile.⁸⁵

Tailoring the buffer gas pressure and/or composition has been shown to improve ion injection efficiency. However, the efficiency of collision-induced dissociation (CID)^{86,87} and the efficiency and resolution of the detected ion signal^{1,88} can also be improved. With this in mind, one enhancement to the idea of a pulsed valve which is limited to on or off would be a variable flow controller. Such a valve would allow the buffer gas pressure to be continuously adjusted during the scan. However, an appropriate valve is difficult to find commercially because the valve must respond quickly (≈ 10 ms) and be capable of providing low flows (≈ 0.01 -50 mL/min).

No matter how the buffer gas pressure or composition is varied during the scan, the major disadvantage of any of these techniques is the time required to pump out the extra buffer gas which was added. The length of the scan becomes very important when the mass spectrometer has been coupled to a chromatographic separation such as gas chromatography, liquid chromatography, or capillary electrophoresis. With these techniques, analytes elute into the ionization source in elution bands ranging from several seconds to less than a second wide. In order to sample these chromatographic peaks adequately, the mass spectrometer must scan fast enough to obtain several mass spectra across the width of the peak. Although pulsed valves have demonstrated gas pulse widths of 10 ms at FWHM, it can take as long as 30 to 50 ms to pump out most of the gas.⁸⁴ With a continuous ionization source, the time required to pump out the added buffer gas might be better spent injecting ions for longer with conventional buffer gas pressures.

Improved Ion Injection Efficiency at Low q_z

Returning to the ion injection simulations shown in Chapter 3, it was interesting to note that m/z 100 was trapped with an efficiency of $\approx 3.5\%$ while m/z 1522 was trapped with a much higher efficiency of 22.6% (see Figure 3-19 and Figure 3-21). There are several differences between the trapping of m/z 100 and 1522. First, m/z 1522 is larger and undergoes collisions more frequently; however, because of the larger mass, these collisions are less efficient in removing kinetic energy. Second, m/z 1522 travels at a significantly lower velocity than m/z 100 and was found to interact more strongly with the RF fringe field as it approached the ion trap. Finally, m/z 1522 is trapped at a lower q_z value than m/z 100 (0.075 versus 0.3). A series of simulations was run to attempt to explain this increase in trapping efficiency and how it might be used to improve the trapping efficiency of all m/z ions.

The results from all of the simulations run for different m/z ions and kinetic energies were compiled. These included ions of m/z 100, 524, 1522, and 3056 as well as several kinetic energies for each m/z . All of these simulations started ions outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with a buffer gas pressure of 1.5 mtorr of helium. The percentage of ten ions injected at different initial RF phases and q_z values was recorded. Table 4-1 shows the m/z ions and kinetic energies studied as well as the approximate velocity of ions entering the ion trap, optimum q_z for trapping, and trapping efficiency at the optimum q_z . Since a linear relationship between the q_z and the maximum velocity of ions was predicted by the pseudo-potential well model (equation 2-18), the optimum q_z for trapping was plotted as a function of the approximate velocity of ions entering the ion trap (Figure 4-2). These velocities are the velocities the ions are

Table 4-1 – List of ions simulated to determine the optimum q_z and the maximum trapping efficiency of each with 1.5 mtorr helium. Kinetic energy and velocity are the approximate values ions have as they enter the ion trap (neglects effects of ion momentum and RF fringe field).

m/z	Kinetic Energy (eV)	Velocity (mm/ μ s)	Optimum q_z	Max. Effic. (%)
100	5.0	3.11	0.170	7.1
100	6.0	3.40	0.180	7.4
100	7.0	3.68	0.195	6.1
100	8.0	3.93	0.205	6.6
100	9.0	4.17	0.215	5.2
524	7.0	1.61	0.105	14.8
1522	5.0	0.80	0.070	44.2
1522	5.5	0.84	0.065	39.7
1522	6.5	0.91	0.070	28.1
1522	7.5	0.98	0.075	27.7
1522	8.5	1.04	0.075	22.0
1522	9.5	1.10	0.080	20.6
3056	4.0	0.50	0.04625	18.9
3056	5.0	0.56	0.048125	100.0
3056	6.0	0.62	0.05250	87.8
3056	7.0	0.66	0.05500	68.6
3056	8.0	0.71	0.05625	58.4

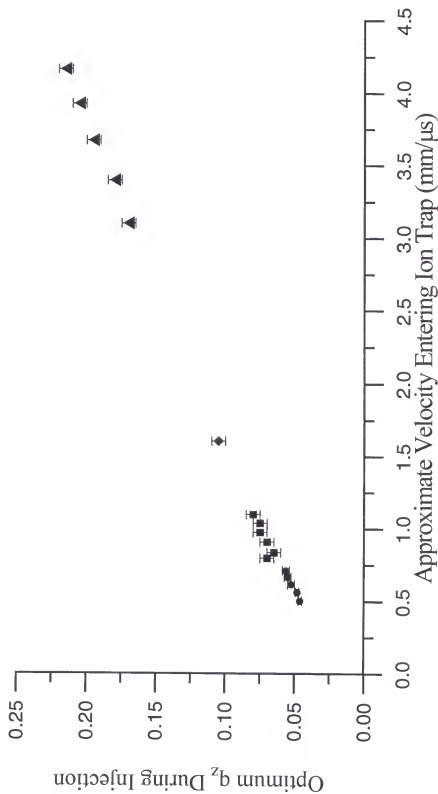


Figure 4-2 – Plot of the simulated optimum injection q_z for ions of m/z 100 ($\blacktriangle$), 524 ($\blacklozenge$), 1522 ($\blacksquare$), and 3056 ($\bullet$) injected at various kinetic energies. The x-axis shows the approximate velocity of the ions as they enter the ion trap neglecting the effects of ion momentum and RF fringe field. The error bars show the simulation step size in q_z .

assumed to enter the ion trap with because of the ions' initial kinetic energies and the offset on the ion trap. These velocities should be regarded as approximate because the RF fringe field affects the velocities of ions as they enter the ion trap, as shown in Figure 3-15. Despite this effect, the optimum q_z appears to be directly related to the velocity of the ions entering the ion trap. An even more interesting plot is one of the maximum trapping efficiency obtained for each m/z versus the optimum q_z during injection (Figure 4-3). In general, ions trapped at lower q_z values (a consequence of them entering the ion trap with lower velocities) are trapped with higher efficiencies. As was shown in Chapter 3, the trapping efficiency was 22.6% for m/z 1522 (Figure 3-21) versus 3.9% for m/z 100 (Figure 3-19). The one exception is the lowest q_z value where the trapping efficiency has dropped dramatically. At the extremely low velocity required for this low q_z , ions do not have sufficient kinetic energy to traverse the RF fringe field. As a result, many of the injected ions are repelled before even reaching the ion trap (as was seen in Figure 3-15c). The most obvious consequence of this is for a constant kinetic energy ion beam (approximately the case for the commercial skimmer design). Higher m/z ions will be trapped with higher efficiencies than lower m/z ions because of their lower velocities. This might partially explain the observation that external ion source ion trap instruments show an abundance of high m/z ions compared to quadrupole mass filter and magnetic sector mass spectrometers.²⁹

If the ion trap does trap ions more efficiently at lower q_z values, it should be possible to inject ions at lower velocities to take advantage of this relationship. To determine if the relationship between trapping efficiency and the velocity of the injected

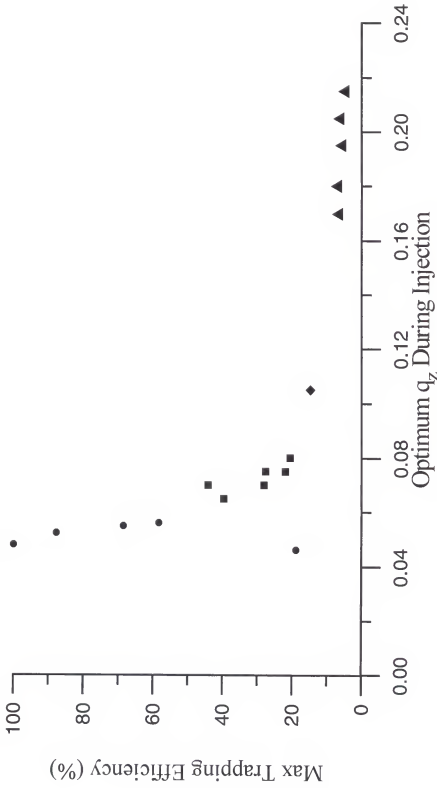


Figure 4-3 – Plot of the simulated maximum trapping efficiency for ions of m/z 100 (▲), 524 (◆), 1522 (■), and 3056 (●) injected at various kinetic energies.

ions is independent of the m/z , high m/z ions were injected at high kinetic energies and low m/z ions were injected at low kinetic energies. Specifically, m/z 1522 was injected at a kinetic energy of 106.54 eV which caused it to enter the ion trap with approximately the same velocity as a standard m/z 100, 7 eV ion. Simulations of m/z 1522 ions started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=103.04$ eV (ions accelerate to 106.54 eV as they enter the ion trap) were performed. The q_z was varied between 0 and 0.9 in 0.005 increments while the starting RF phase was varied between 0° and 359° in 1° increments. The resulting contour plot of the percentage of ions trapped, shown in Figure 4-4a, can be compared to the standard case of 7 eV, m/z 100 ions in Figure 4-4b. The m/z 100 ions at 106.54 eV were found to be trapped with an efficiency of 4.68% at a q_z of 0.195. These are similar to the values for the m/z 100, 7 eV ions of approximately the same velocity. These two contour plots are not exactly the same, indicating there is some effect from the m/z of the ion and the different influence of the RF fringe field for the two cases. However, the contour plots are similar enough to infer that the velocity with which an ion enters the ion trap is important in determining the q_z and RF phases at which ions are trapped. The s-shaped curve of the 7.5 eV, m/z 1522 (see Figure 3-14) has become bullet-shaped because of the higher velocity with which the ion was injected.

To further study this effect, a m/z 100 ion was injected at approximately the same velocity as the m/z 3056, 5 eV ions which were trapped with 100% efficiency. Ions of m/z 100 ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV in the octopole held at a DC offset of -6.5 V. The ion trap was held at a DC offset of -3.163613 V so that the ions entered the ion trap with

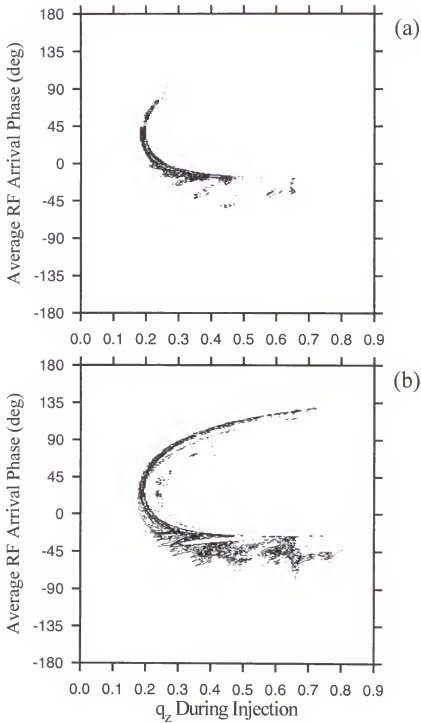


Figure 4-4 – Contour plots of the percentage of ions trapped for two different m/z ions injected at approximately the same velocity (3.68 mm/ μ s if no RF voltage on the ring). (a) m/z 1522 injected at 106.54 eV. (b) m/z 100 injected at 7 eV.

approximately 0.163613 eV. The q_z was varied between 0.0275 and 0.04 in 0.00125 increments while the starting RF phase was varied between 0° and 359° in 1° increments. The resulting contour plot of the percentage of ions trapped is shown in Figure 4-5a. For comparison, ions of m/z 3056 were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=1.5$ eV in the octopole held at a DC offset of -6.5 V. The ion trap was held at a DC offset of -10 V so that the ions entered the ion trap with approximately 5 eV. The q_z was varied between 0.04525 and 0.05025 in 0.00125 increments while the starting RF phase was varied between 0° and 359° in 1° increments. The resulting contour plot of the percentage of ions trapped is shown in Figure 4-5b. Interestingly, the m/z 100 ions at 0.163613 eV were found to be trapped with an efficiency of 56.4% instead of 6.1% for the standard case of 7 eV ions. The efficiency is not as high as for the m/z 3056 ions at 5 eV presumably because of differences in ion momentum. Also, the RF voltages applied to the ring electrode are vastly different for the two m/z ions meaning the ions are affected to different extents by the RF fringe field as they approach. As a result, these two m/z ions do not enter the ion trap with exactly the same velocity, partially explaining the difference in the optimum q_z for the two cases. From the results shown in Figure 4-5a, the m/z 100 ion beam injected at approximately 0.16 eV would be trapped at a $q_z=0.0375$, which translates to a LMCO of 4.2. This is an incredibly low RF voltage corresponding to only about 19 V_p of RF voltage on the ring electrode.

It appears that injecting ions at extremely low velocities has the potential of increasing the trapping efficiency. Low velocity injection may have the added benefit of reducing the amount of fragmentation of injected ions.^{29,43,80} However, the simulations

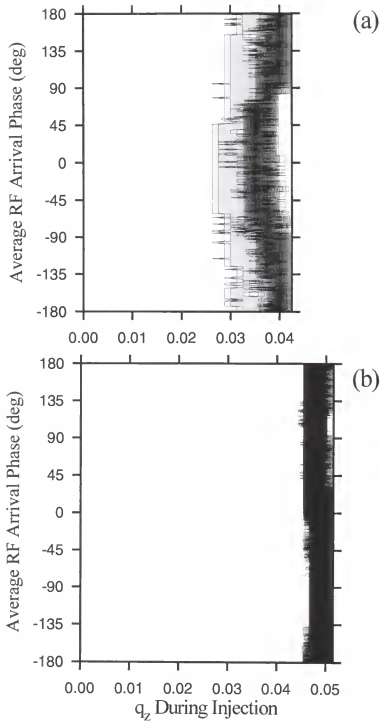


Figure 4-5 – Contour plots of the percentage of ions trapped for two different m/z ions injected at approximately the same velocity (0.56 mm/ μ s if no RF voltage on the ring). (a) m/z 100 injected at 0.16163 eV. (b) m/z 3056 injected at 5 eV.

suggest that the LMCO during injection is very critical. Ions were only trapped between a q_z of 0.035 and 0.040 which corresponds to a LMCO between 3.9 and 4.4. This is not only a very low RF voltage, but the optimum is very narrow meaning it may be difficult to obtain experimentally. In addition, an ion beam may not be capable of being efficiently transported at such a low kinetic energy. It might be possible to transport the ion beam at relatively high kinetic energies and then abruptly decelerate it as it enters the ion trap (as was done in the simulation of m/z 100 at 0.16 eV). The challenge would be to minimize ion losses as the ion beam is decelerated and tends to defocus. Without experimental data it is unknown whether any increase in trapping efficiency can overcome any ion losses due to ion focusing problems. The prediction of such a method from the computer simulation is still valuable because it suggests the ion injection model which has been developed is giving a return on its investment. Such a model is valuable when it not only explains trends observed experimentally, but also suggests new experiments.

Up to this point, the trapping efficiency at low q_z is assumed to increase because the number of efficient RF phases for a given q_z increases. This is the fortunate consequence of the opening of the bullet-shape into an s-shape and eventually into a vertical line. However, the reason for this increase in the phase acceptance still has not been explained. One possible explanation is the interaction of the ion beam with the RF fringe field as was discussed in Chapter 3. However, this cannot be the only process at work since m/z 1522 ions started inside the ion trap (see Figure 3-13b) show evidence of increased phase acceptance as well over m/z 100 ions (although not to the extent of ions started outside). In addition to the RF fringe field effect, the increase in phase acceptance

may be a consequence of the lower q_z values used during injection. To examine this in more detail, the concept of phase space dynamics will be introduced.

Phase Space Dynamics

Phase space dynamics is a useful technique to study the transfer of collections of charged particles, ions in this case, from one place to another.⁸⁹ Manipulating an ensemble of ions involves the modification of the velocity and position distribution of the ensemble.⁹⁰ Phase space encompasses a full six dimensions, three velocity coordinates and the corresponding three position coordinates (other equivalent representations include momentum/position and energy/time). It is difficult to visualize this full six-dimensional representation, so phase space is often shown in the form of action planes which are two-dimensional phase space plots of the velocity in a particular coordinate direction versus the corresponding position in that coordinate.

The effect of interactions between the ions (ion-ion interactions or space charge) is normally considered insignificant compared to the effect of the applied electric fields;⁹⁰ this allows the Liouville theorem to be applied. This theorem states that when linear fields are involved, the overall phase space volume of the particle ensemble will be conserved.⁸⁹⁻⁹² In phase space, the ensemble behaves as an incompressible fluid. Transferring ions efficiently from one place to another is accomplished by matching the phase space volume of the ensemble of ions to the phase space volume of the collection device.⁹² At this point it should be emphasized that the term “phase” in phase space has no relationship to angle or RF phase; in this case, phase refers to a stage of development. In other words, the phase space plot for an ensemble of ions can continuously change as it progresses through different phases in its development.

At this point, it would be useful to present some phase space, or action diagrams, of the ion trap. As will be seen, phase space provides a powerful technique for calculating the maximum positions and velocities for trapped ions. Several excellent reviews of phase space dynamics have been written^{14,16} so only the relevant details will be explained here. Essentially, a phase space plot is a plot of velocity in a given direction versus the position in the same direction. At a particular RF phase, ϕ_{RF} , each ion will have a position u and velocity $\dot{u}$ which will lie on an ellipse in phase space. As the RF phase varies, these ellipses vary in shape and orientation, but the areas of the ellipses remain constant. A typical ellipse, termed an acceptance ellipse, for a given RF phase is shown in Figure 4-6. The shape of these ellipses is given by the general equation

$$\Gamma u^2 + 2Au\dot{u} + B\dot{u}^2 = \epsilon \quad (4-1)$$

where A , B , and Γ are constants determined by the RF phase and ϵ is the ellipse geometry. These ellipses define the maximum velocity an ion can have at a particular excursion for a given RF phase. The underlying principle of phase space is once an ion has a position and velocity inside an acceptance ellipse, it will undergo a stable trajectory indefinitely. This makes phase space a powerful technique for calculating ion stability since all that matters is the position and velocity of an ion at a given moment in time; its history is unimportant. Once an acceptance ellipse is calculated, it can be scaled in position and velocity to increase the area inside the ellipse, but maintaining the ratio of the major and minor ellipse axes. The acceptance ellipse can be increased in size until the ellipse has expanded to the physical boundary of the device. This discussion has so

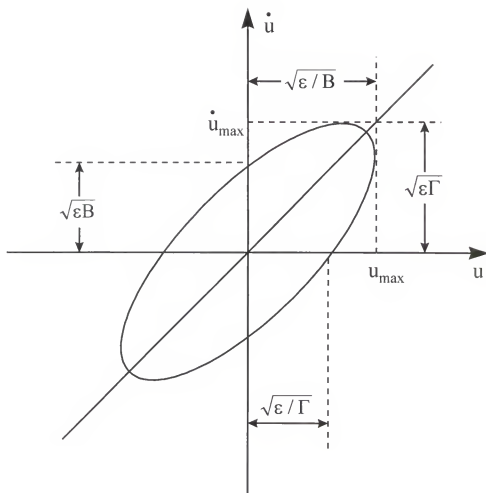


Figure 4-6 – Elliptical boundary of phase space showing the one-dimensional acceptance of the ion trap at a particular RF phase. Adapted from reference 14.

far made the assumption of a pure quadrupole field inside the ion trap. For now, some acceptance ellipses will be presented assuming a pure quadrupole field; however, in the next section the effect of higher-order fields will be discussed.

The point of introducing the concept of phase space dynamics was to propose an explanation for the increased trapping efficiency at low q_z . Several acceptance ellipses were generated using SIMION to demonstrate the effect of q_z on phase space. Ions of m/z 100 were started at the center of an ion trap (with endcap holes) at a kinetic energy appropriate to cause a maximum axial excursion of approximately 1 mm. The axial position and velocity of the ions were sampled at eight RF phases of -180° , -135° , -90° , -45° , 0° , 45° , 90° , and 135° each RF period to generate phase acceptance ellipses for these eight RF phases. This was done for q_z values of 0.6, 0.3, and 0.04; the resulting acceptance ellipses for the eight RF phases are plotted in Figure 4-7. Assuming the RF field is approximately quadrupolar, the positions and velocities were scaled linearly so that the maximum position became the confines of the device (z_0). At higher q_z , the phase acceptance ellipses vary dramatically with RF phase, while at lower q_z they are more consistent. An injected ion has a large axial excursion as well as a large axial velocity. Compared to higher q_z values, an ion injected at low q_z is likely to fall inside more phase acceptance ellipses; this larger phase acceptance will translate to a higher trapping efficiency. Remember that once an ion has a position and velocity inside the acceptance ellipse for the RF phase at that time, the ion can be considered trapped. By injecting ions at low enough velocities for these low q_z values, it may be possible to take advantage of this increased phase acceptance.

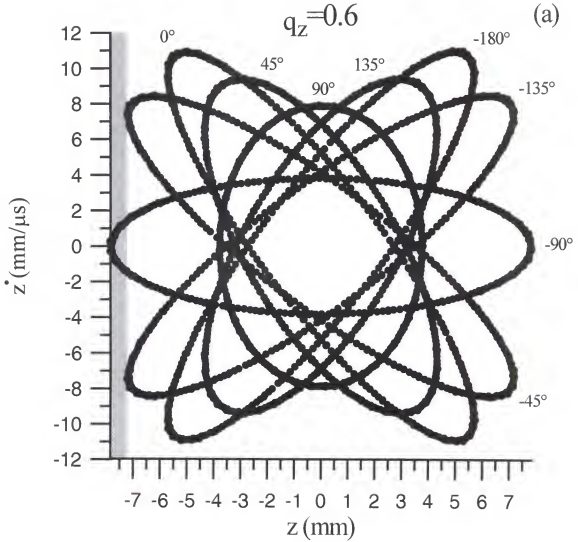


Figure 4-7 – Phase space plots showing acceptance ellipses for (a) $q_z=0.6$, (b) $q_z=0.3$, (c) $q_z=0.04$. The number of phase ellipses which encompass areas of large axial excursions (shaded portion) is higher for the lower q_z values. Note that while the x-axes for the three plots are the same, the y-axes are different.

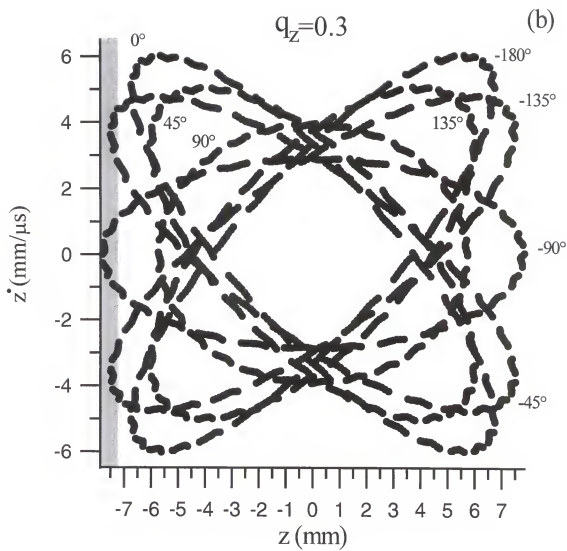


Figure 4-7 – continued.

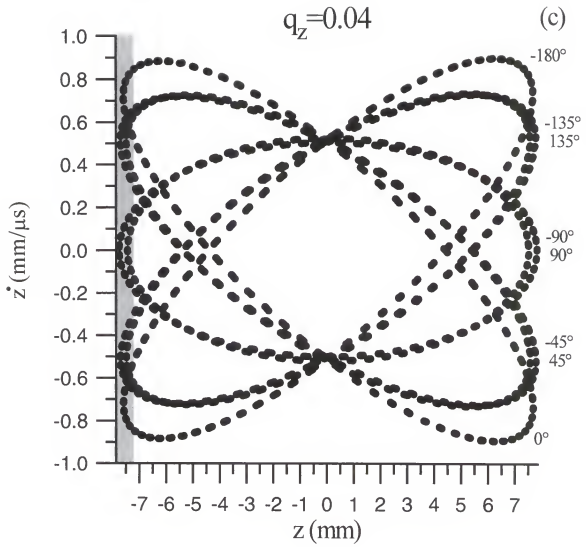


Figure 4-7 – continued.

Phase space can also be used to understand why injected ions cannot be trapped indefinitely; without some method of removing kinetic energy, the maximum position and velocity of ions in phase space remains constant. The definition of trapping is that a particle must return to a position arbitrarily close to its starting position.⁹³ By definition, an injected ion cannot be trapped since its starting position is outside the ion trap. In other words, ions will be lost from the ion trap when they again find the phase space location through which they entered in the first place.⁹² This can be prevented by collisional damping, which decreases the velocity of the ions and in turn reduces the maximum excursions; in effect, phase space shrinks. Another way of postponing the time which ions leave the ion trap is to transfer some of the axial kinetic energy of the ions into radial kinetic energy. The distorted field around the endcap holes has many higher-order field components which provide efficient coupling between axial and radial modes⁹². This coupling transforms the phase space volume so that fewer ions are immediately lost to the endcap electrodes and those which remain have sufficient time to be collisionally damped. As was shown in Chapter 3, the longer an ion remains in the ion trap, the more likely sufficient kinetic energy will be lost through collisions to trap the ion indefinitely. In addition, the endcap holes were seen to allow ions to be trapped over a second range of RF phases (see Figure 3-5). These higher-order fields around the holes distort the shape of the phase acceptance ellipses and make them a function of position so that the scaling of the acceptance ellipses is no longer valid.

Phase Space Manipulation of Ion Beams

Returning to the basics of phase space dynamics, transferring ions efficiently from one place to another is accomplished by matching the phase space volume of the ensemble of ions to the phase space volume of the collection device.⁹² So far, the methods of improving the trapping efficiency from continuous ionization sources presented in this chapter have focused on increasing the phase acceptance of the ion trap by using higher pressures of buffer gas or injecting at low q_z values. However, an alternative method would be to manipulate the ion beam itself to make it a better match to the existing phase space acceptance of the ion trap. In this section, a brief introduction to the phase space manipulation of ion beams is presented.

Two events are necessary for an injected ensemble of ions to be trapped successfully. First, the ensemble must be focused in the radial direction so the beam passes through the endcap hole; an example of this is shown in Figure 4-8. Here, the ion beam is focused in the y direction in order to be narrow enough to fit through the 0.060 in endcap hole. Because phase space is incompressible when linear fields are used, the overall phase space volume is preserved.

Getting the ions through the hole in the endcap is only the first step. The second requirement is that the ensemble of ions must arrive during an acceptable RF phase window. Previously, methods were described which intend to widen this phase acceptance window. Alternatively, a set of appropriate ion optics could be used to temporally focus an ion beam so that the ensemble of ions arrives at the ion trap during an RF phase efficient for trapping.^{7,90} The manipulation of phase space for this process is

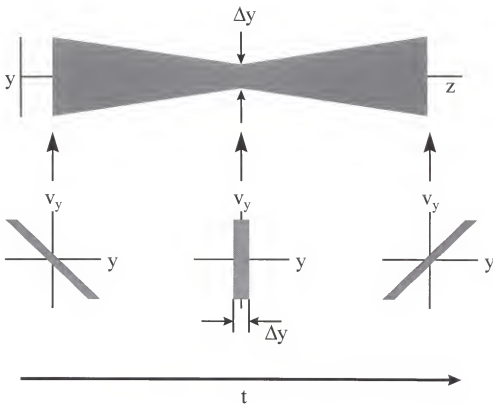


Figure 4-8 – Representation of an ion beam which is traveling toward an ion trap. The ion beam is focused in the y -direction to fit through the endcap hole. Below, corresponding phase space diagrams are shown representing the changes to phase space ellipses as a result of the spatial focusing. Adapted from reference 28.

shown in Figure 4-9; in this case it is more convenient to represent phase space in terms of kinetic energy versus time. If the voltages applied to the ion optics are carefully chosen and timed, the time focus will occur at the entrance endcap hole. However, the only way to achieve this temporal focus is to begin with an ion beam which has a kinetic energy spread. This can be done in such a way that ions further from the ion trap are given higher kinetic energies so that they catch up with the slower moving ions in front of them and came into temporal focus. This means that the ions will arrive at the endcap hole over a narrower range of times, but they will have a wider range of kinetic energies when they get there.

From this basic concept, Moore and colleagues have proposed a method of “phase bunching” to improve trapping efficiency from continuous ionization sources.^{7,90,91} In their approach, a continuous beam of ions would be bunched into a narrow time packet synchronized to arrive during a favorable RF phase window. They have proposed using a bunching cavity placed in front of the entrance endcap which would bunch the continuous ion beam into ion pulses which arrive every 20 μ s. With this system the authors hoped to be able to obtain trapping efficiencies of greater than 90%. However, this phase space manipulation is not trivial; to date, no reports of successful “phase bunching” have been reported. To focus temporally the ion beam, the kinetic energy distribution must be increased. This increased kinetic energy distribution changes the RF phase acceptance window (as will be discussed in more detail in the remainder of this chapter).

To study other methods of manipulating the ion beam as it approached the ion trap, the simulations of injected ions presented in Figure 3-18 were revisited. Preliminary work focused on m/z 100 which had the most room for improvement in trapping

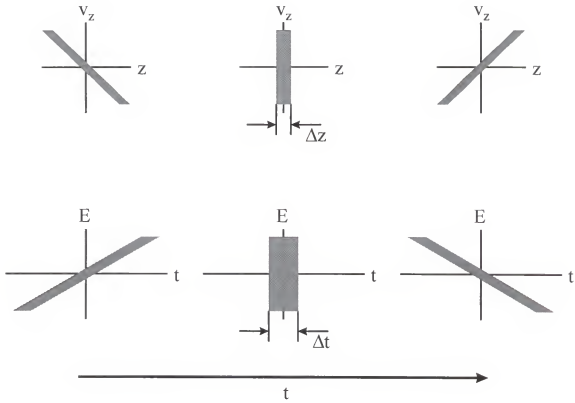


Figure 4-9 – Phase space diagrams showing an ion beam going through a time focus. Phase space is shown in conventional velocity-distance space as well as energy-time space. The time focus occurs in the middle plot; however, this time focus resulted because the ion beam started with a wide kinetic energy distribution. Adapted from reference 28.

efficiency. At a given q_z , 0.25 for example, ions of different kinetic energy are trapped at different RF phases as indicated by a shift in the bullet shaped curve. This relationship between kinetic energy and RF phase is explored in the remainder of this chapter as a method of improving trapping efficiency.

Desired Relationship Between Kinetic Energy and RF Phase

Simulations in the literature have shown a relationship between the kinetic energy of injected ions and the RF phases which are favorable for trapping.^{7,53} However, these simulations did not take into account the effects of endcap holes, so SIMION simulations were run to characterize the relationship between kinetic energy and RF phase for the LCQ ion trap. Since the kinetic energy and RF phase of ions at the time they enter the ion trap were of interest, ions of m/z 100 were started at the inner plane of the entrance endcap ($z_{init}=7.85$ mm, $x_{init}=0$ mm, $y_{init}=0$ mm, and $\Theta=5^\circ$) with various initial kinetic energies between 0 and 14 eV. At a q_z of 0.25, ten ions were injected at each RF phase between 0° and 359.8° in increments of 0.2° . The percentage of ions trapped at each of these initial RF phases is shown for six different kinetic energies in Figure 4-10. As the initial kinetic energy of the ions is increased, the ranges of efficient RF phases shift closer to 0° . Looking at these data, there is an obvious relationship between the kinetic energy an ion has and the RF phases at which it can be trapped. From the data in Figure 4-10, the desired variation of the kinetic energy with RF phase was constructed. Figure 4-11 shows a plot of injection kinetic energy versus initial RF phase. At each kinetic energy, the horizontal bars indicate the range of RF phases over which $\geq 10\%$ of the ions were trapped. If it were possible to introduce the ions with the proper kinetic energy for the RF

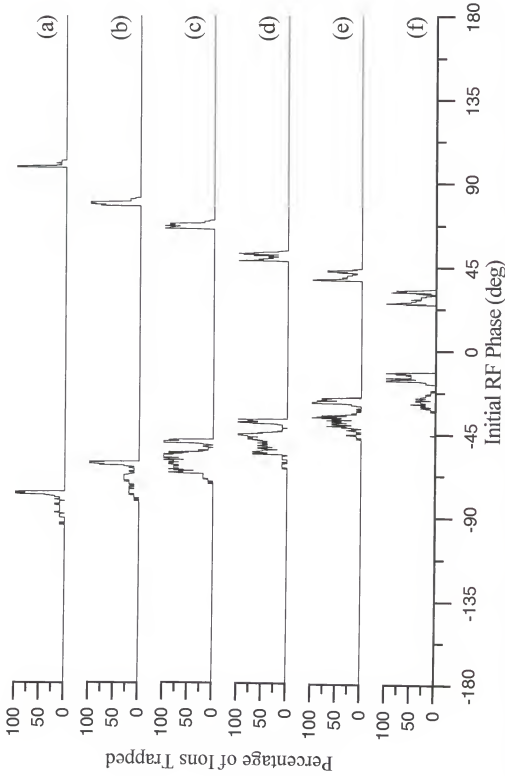


Figure 4-10 – Percentage of m/z 100 ions trapped at $q_z=0.25$ and different initial RF phases for six different initial kinetic energies (a) 1 eV, (b) 3 eV, (c) 5 eV, (d) 7 eV, (e) 9 eV, and (f) 11 eV.

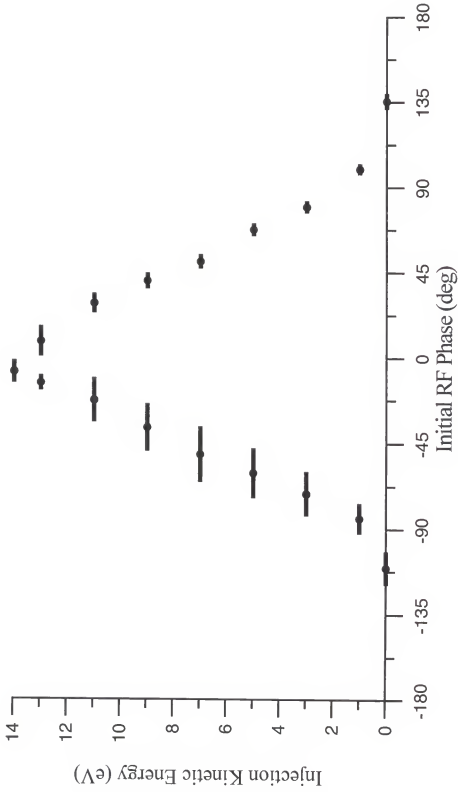


Figure 4-11 – Desired variation of injection kinetic energy with initial RF phase of m/z 100 ions started at endcap boundary. $q_z=0.25$. Horizontal bars indicate range of RF phases over which $\geq 10\%$ of ions were trapped.

phase at which they arrive (or to arrive at the correct RF phase for the kinetic energy they have), a higher percentage of ions could be trapped.

Phase-Sympathetic Injection

Based on the relationship between the kinetic energy and RF phase shown in Figure 4-11, a novel technique termed phase-sympathetic injection was developed. Basically, this technique uses periodic time-varying voltages to manipulate the kinetic energy and arrival time of the ions so that they arrive at the entrance endcap with a kinetic energy appropriate for that particular RF phase.⁴ This technique is similar to the idea of “phase bunching” proposed by Moore and colleagues in a series of articles.^{7,90,91} In their approach, a continuous beam of ions would be bunched into a narrow time packet which would be synchronized to arrive during a favorable RF phase window. However, this phase space manipulation is not trivial because ions must be temporally focused without significantly increasing the kinetic energy distribution. On the other hand, phase-sympathetic injection seeks to alter the kinetic energy and/or the RF phase at which ions arrive at the ion trap, making the ion optics and electric fields much simpler.

When the relationship between kinetic energy and RF phase shown in Figure 4-11 was first plotted, it was unknown whether such a manipulation of the ion beam was even possible. After all, phase-sympathetic injection seeks to manipulate the ion beam on the time scale of an RF period (1.316 μ s). Since phase-sympathetic injection seeks to control the kinetic energy of the ion beam as it enters the ion trap as a function of RF phase, it made sense to vary the offset voltage on the ion trap as a function of RF phase.

Applying an AC Offset to the Ion Trap

In the standard operation of the ion trap a DC offset voltage, V_{TrapDC} , is applied to the ion trap so that ions are efficiently transmitted into the ion trap. This offset determines the final potential of the ions and therefore their final kinetic energy. The kinetic energy of the ion beam could be varied as a function of RF phase if the trap offset were varied as a function of RF phase. In the simplest realization, a sinusoidal voltage at the same frequency as the RF drive voltage could be applied to all three trap electrodes in addition to the standard DC offset. This AC offset, V_{TrapAC} , would make the final potential of the ion trap, and therefore the kinetic energy of the ion beam, a function of RF phase. Equation 4-2 shows the voltage applied to the ring electrode as the summation of the standard RF trapping voltage, a DC offset, and an AC offset. Note that V_{TrapAC} is phase shifted from the RF drive voltage by ϕ_{AC} . Equation 4-3 shows the voltage applied to each of the endcap electrodes and is the summation of the standard DC offset and the AC offset.

$$V_{\text{Ring Electrode}} = \frac{-q_z m (r_o^2 + 2z_o^2) \Omega^2}{8e} \sin(\Omega t) + V_{\text{TrapDC}} + V_{\text{TrapAC}} \sin(\Omega t + \phi_{\text{AC}}) \quad (4-2)$$

$$V_{\text{Endcap Electrodes}} = V_{\text{TrapDC}} + V_{\text{TrapAC}} \sin(\Omega t + \phi_{\text{AC}}) \quad (4-3)$$

By applying the AC offset to all three electrodes, ions inside the ion trap are not affected. This is a requirement in order to be able to accumulate ions from a continuous ion beam.

In a simple model of ion injection, the standard operation of the ion trap with just V_{TrapDC} should produce an ion beam which enters the ion trap with a kinetic energy constant with RF phase (see Figure 4-12a). This arrival kinetic energy is calculated by

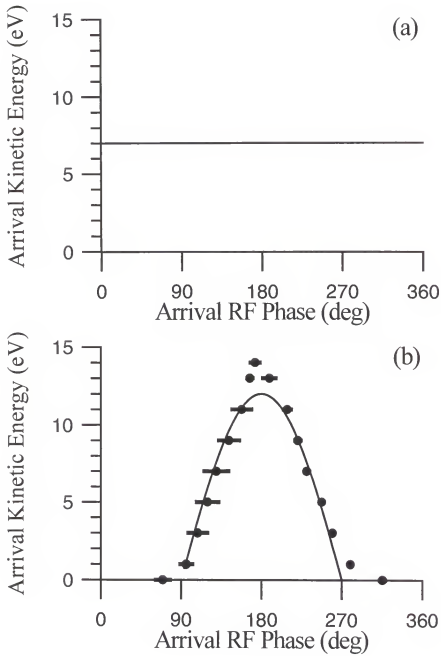


Figure 4-12 – Expected variation of kinetic energy with RF phase.
 (a) For standard operation with $V_{\text{TrapDC}} = -10$ V and $V_{\text{TrapAC}} = 0$ V_p.
 (b) With $V_{\text{TrapDC}} = -3$ V, $V_{\text{TrapAC}} = 12$ V_p, and ϕ_{AC} . Desired variation from Figure 4-11 shown superimposed.

simply subtracting the potential of the ion trap from the starting potential of the ion beam. From the studies in Chapter 2, the ion beam appears to be formed at a potential of -3 V; with the standard V_{TrapDC} of -10 V applied to the trap, ions should enter with 7 eV of kinetic energy. In contrast, when the AC offset is applied and the potential is now the sum of V_{TrapDC} and V_{TrapAC} , the kinetic energy of the ions entering the trap should be a function of RF phase (see Figure 4-12b). Values of $V_{\text{TrapDC}}=-3$ V, $V_{\text{TrapAC}}=12$ V_p, and $\phi_{\text{AC}}=90^\circ$ were calculated to create a kinetic energy versus RF phase profile which approximated the desired relationship shown in Figure 4-11.

This is not the kinetic energy versus RF phase relationship which is obtained when ions are started outside the ion trap, however. One of the reasons ions do not arrive at the ion trap with the kinetic energy predicted in Figure 4-12 is that ion momentum tends to resist fast changes in kinetic energy. In addition, RF field penetration has a strong effect on ions, as was seen in Chapter 3. These effects can be seen from the results of a computer simulation where m/z 100 ions were started outside the ion trap ($z_{\text{init}}=19$ mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV. The user program was modified to record the RF phase at which ions cross the inner plane of the entrance endcap $z=z_0$ (the arrival RF phase) and the corresponding kinetic energy (the arrival kinetic energy). Figure 4-13a shows the RF phase ions arrive at versus the RF phase they started with outside the ion trap. Ions arrive after an approximately constant transit time, regardless of RF phase. Figure 4-13b shows the kinetic energy ions arrive with versus the arrival RF phase. It was predicted that this would be constant, but because of RF field penetration, ions are speeded up or slowed down causing them to arrive with a kinetic energy which is strongly dependent on the RF phase. Remember, no AC offset is being

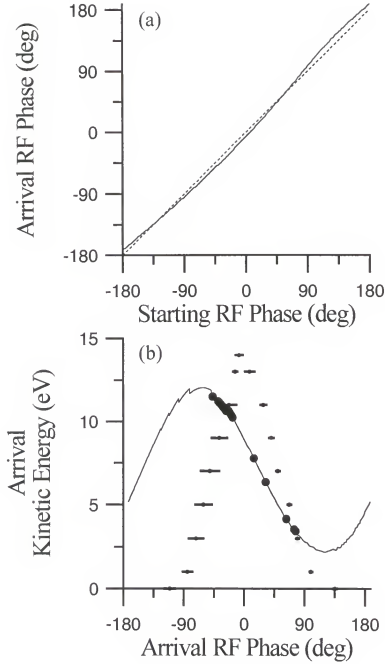


Figure 4-13 – Simulated variation of (a) the arrival RF phase versus the starting RF phase and (b) the arrival kinetic energy versus the arrival RF phase. Standard operation of $V_{\text{TrapDC}} = -10$ V and $V_{\text{TrapAC}} = 0$ V_p. m/z 100, $q_z = 0.25$, $E_0 = 3.5$ eV (ions enter the ion trap with 7 eV).

applied; this variation is caused by the RF fringe field. Only minimal distortion in the arrival RF phase was seen in Figure 4-13a because the change in kinetic energy occurred very close to the inner plane of the entrance endcap; therefore, there was not enough time for the kinetic energy change to cause a large change in arrival time. The desired profile from Figure 4-11 is shown superimposed in Figure 4-13b; the solid circles indicate which conditions resulted in $\geq 10\%$ of the ions being trapped. There is only minimal overlap with the desired profile and only a small fraction of the ions are successfully trapped. From this example, it is clear that any attempt to manipulate the kinetic energy/RF phase relationship of the ion beam must take into account the effects of RF field penetration on approaching ions.

Various values of V_{TrapDC} , V_{TrapAC} , and ϕ_{AC} were simulated to determine which combinations could increase the trapping efficiency by yielding the desired kinetic energy/RF phase relationship. Early on, it was suspected that the AC offset applied to the entrance endcap was adversely affecting ions as they approached the endcap. To minimize these effects, a lens was added between the second octopole and the entrance endcap (see Figure 4-14b). With only DC applied to this lens, it acted as a shield and prevented ions from interacting with the AC offset applied to the entrance endcap until the ions were close to the ion trap. From this point on, all simulations were performed with this lens in place. For most simulations a DC offset, V_{LensDC} , of -8 V was applied to the lens.

Computer Simulations of an AC Offset Applied to the Ion Trap

To establish a baseline trapping efficiency, simulations were run with the lens in place and no AC offset applied. Ions of m/z 100 were started outside the ion trap ($z_{\text{init}}=19$

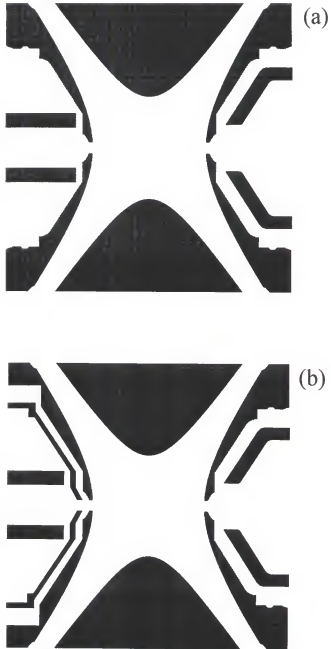


Figure 4-14 – SIMION electrode grids of (a) standard LCQ electrode configuration and (b) with a lens added between the octopole and the entrance endcap to shield ions from AC offset.

mm, $x_{\text{init}}=0.2$ mm, $y_{\text{init}}=0$ mm, and $\Theta=0^\circ$) with $E_0=3.5$ eV (ions enter trap with approximately 7 eV). A q_z of 0.25 was used and a series of ten ions were started at each RF phase between 0° and 359° in increments of 2° . From these simulations, the trapping efficiency was found to be 3.1%. Next, the same experiments were performed for ϕ_{AC} values between 0° and 337.5° in increments of 22.5° and V_{TrapAC} values of 5 V_p , 10 V_p , and 15 V_p . The results are shown in Figure 4-15. The simulation results indicate that for V_{TrapAC} values of 5 V_p and 10 V_p , certain ϕ_{AC} phase differences resulted in improvements in trapping efficiency relative to that with $V_{\text{TrapAC}}=0$ V_p .

To see exactly what effect the AC offset is having on the ions, simulations were run for the case of $V_{\text{TrapAC}}=10$ V_p and $\phi_{\text{AC}}=112.5^\circ$. Ions were started outside the ion trap and the kinetic energy and time ions arrived at the inner plane of the entrance endcap were recorded. The varying trap offset dramatically distorted the arrival time of the ions (see Figure 4-16a) from what was seen without the AC offset (see Figure 4-13a). In addition, a plot of the arrival kinetic energy versus the arrival RF phase is shown in Figure 4-16b. This is shown compared to the desired profile from Figure 4-11; the conditions for which ions are trapped with $\geq 10\%$ efficiency are shown with solid circles. In contrast to the standard case of $V_{\text{TrapAC}}=0$ V_p , the application of the AC offset has produced a kinetic energy/RF phase relationship closer to the desired profile. As a result, three and a half times more ions were trapped. With these encouraging simulation results, the hardware and software was designed to test this technique experimentally.

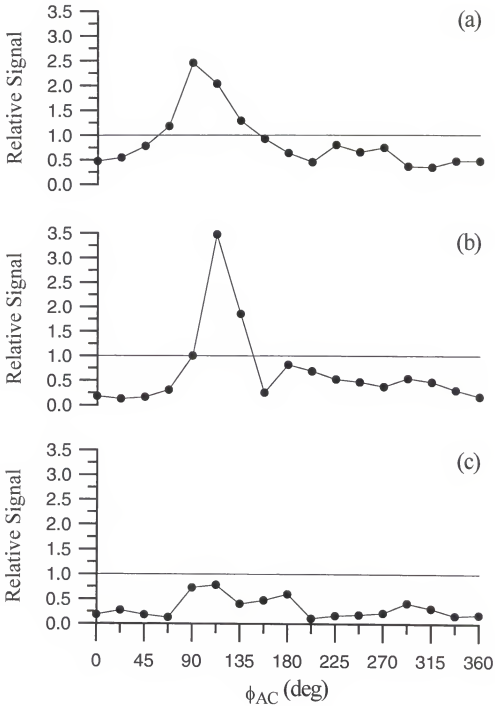


Figure 4-15 – Simulations of m/z 100 showing relative trapping efficiency as a function of ϕ_{AC} for V_{TrApAC} of (a) $5 V_p$, (b) $10 V_p$, and (c) $15 V_p$. Trapping efficiency relative to $V_{TrApAC}=0 V_p$.

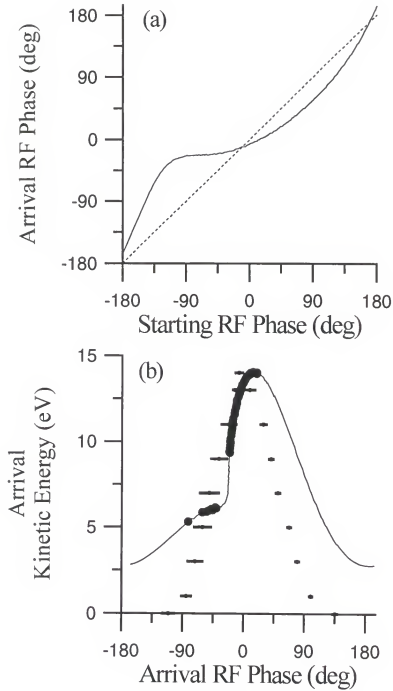


Figure 4-16 – Simulated variation of (a) the arrival RF phase versus the starting RF phase and (b) the arrival kinetic energy versus the arrival RF phase.

$V_{\text{TrapAC}}=10 \text{ V}_p$, $\phi_{\text{AC}}=112.5^\circ$, and $V_{\text{TrapDC}}=-10 \text{ V}$. m/z 100, $q_z=0.25$, $E_0=3.5 \text{ eV}$.

Experimentally Applying AC Offset to the Ion Trap

All experiments in this chapter were performed using the commercial skimmer design and a q_{ej} of 0.9 which resulted in a m/z range of 1850. Applying the AC offset to vary the trap offset was not a trivial experiment; John E.P. Syka at Finnigan MAT was very helpful in the design of the necessary circuitry. Applying the AC offset to the ion trap can be addressed in two stages. First, circuitry was built which applied the AC offset to both endcap electrodes. This was done by modifying a standard LCQ balun circuit (located on the Analyzer Auxiliary PCB) to allow the AC offset to be applied to both endcaps in-phase. This is in contrast to the standard resonant excitation / ejection circuitry which applies the waveform to the endcaps so they are 180° out-of-phase. This circuitry for the AC offset was complicated by RF which capacitively coupled from the ring electrode to the endcaps.

Capacitively Coupled RF on the Endcap Electrodes

The percentage of RF which couples to the endcaps is shown as a function of the ring RF voltage in Figure 4-17. Approximately 0.18% of the RF on the ring appears on the endcaps. A higher percentage of RF appeared to couple at low RF voltages; however, this may be an artifact of noise in the oscilloscope measurements at low voltages. Normally, transformer T2 (see Figure 4-18) protects the resonant excitation / ejection amplifier from this capacitively coupled RF by rejecting common mode signals which appear on both endcaps. This approach cannot be used for the AC offset because that signal is applied in-phase to both endcaps and a transformer arrangement similar to T2 would not be able to differentiate between the AC offset and capacitively coupled RF. Instead, a circuit was designed to null the RF which capacitively couples to the endcaps

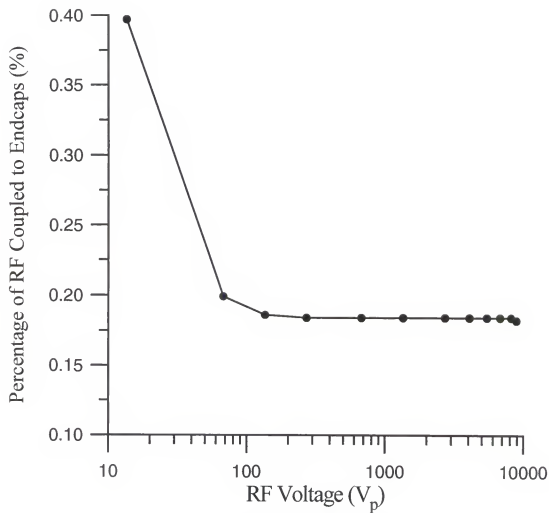


Figure 4-17 – Percentage of RF on the ring electrode which capacitively couples to the endcap electrodes.

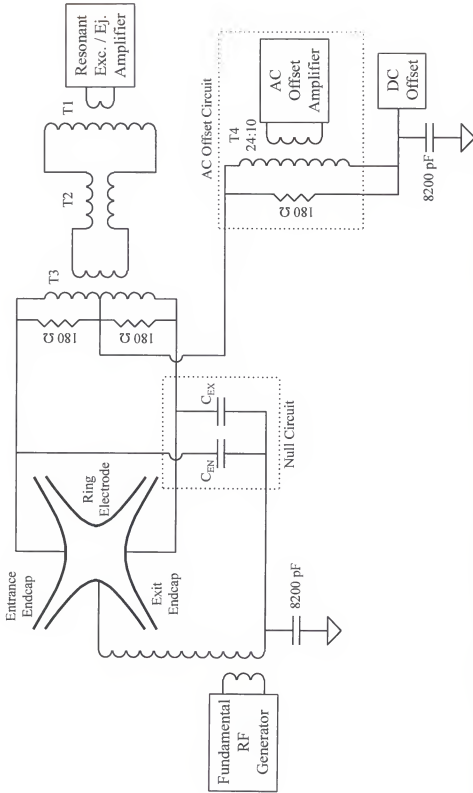


Figure 4-18 – Modified LCQ balun circuit to allow AC offset waveform to be applied in-phase to both endcaps. Also shown is added null circuit to reduce the amount of RF which capacitively couples from the ring electrode to the endcaps.

from the ring electrode, thereby eliminating the problem. The null circuit shown in Figure 4-18 was built and the values of the nulling capacitors C_{EN} and C_{EX} were adjusted until the amount of ring RF which appeared on the endcaps was at a minimum (as measured with an oscilloscope attached to the endcaps). This occurred with $C_{EN}=C_{EX}=2415$ pF, reducing the amount of coupled RF by 38 dB to only 0.0024%.

The addition of this null circuit had an interesting side effect of shifting the m/z calibration of the instrument (see mass spectra in Figure 4-19). With the null circuit installed, ions appeared at lower m/z as evidenced by a change in the mass calibration slope m and intercept b .

$$(m/z)_{\text{actual}} = m \cdot \text{RFDAC} + b \quad (4-4)$$

Without the null circuit, m was 34.286315 and b was 91.717809, while with the null circuit m was 34.215842 and b was 84.647752. The ions were being ejected sooner with the null circuit making it appear as if nulling the RF on the endcaps caused the q_z of the ions to increase. This hypothesis was tested by measuring the frequencies of motion of two different m/z ions. This was done by applying a series of different frequencies to the endcaps (dipolar excitation). When the applied frequency matched the frequency of motion of the ions, ions were resonantly ejected and a decrease in detected ion signal resulted. A plot of the detected intensity versus the applied frequency showed a dip at the frequency of the ions (see Figure 4-20); the measured ion frequency was defined as the midpoint between the frequencies for which 90% of the ions were ejected in this dip. When the null circuit was added, the secular frequency of the ions increased. This makes sense, since the RF which coupled to the endcaps was in-phase with the RF on the ring electrode. The q_z of the ions is determined by the potential difference between the ring

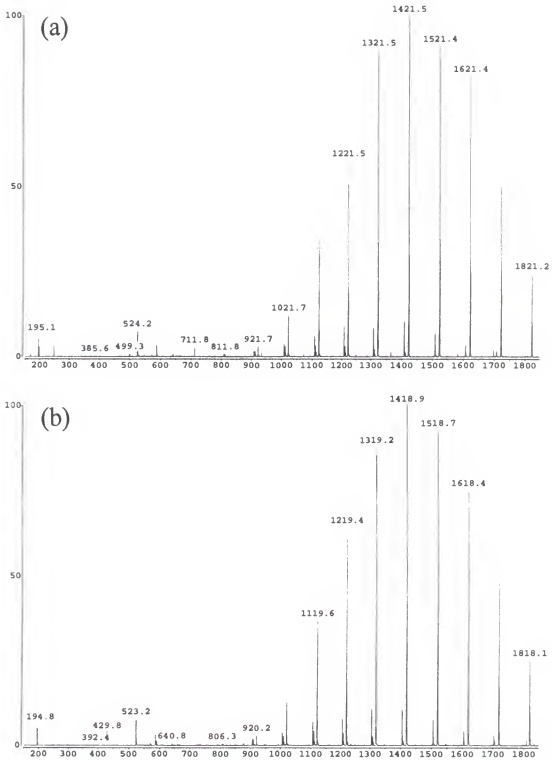


Figure 4-19 – Mass spectra of mixture of caffeine (m/z 195.1), met-arg-phe-ala (m/z 524.3), and Ultramark 1621 (m/z 922, 1022, 1122, 1222, 1322, 1422, 1522, 1622, 1722, 1822, and 1922) (a) without null circuit and (b) with null circuit.

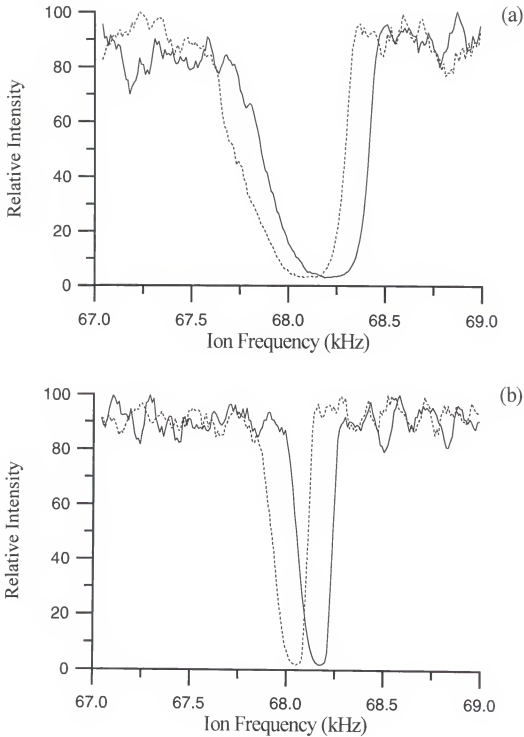


Figure 4-20 – Ion frequency measurements with (solid line) and without (dotted line) null circuit for (a) m/z 195.1 and (b) m/z 1522 held at a q_z of approximately 0.25.

and endcap electrodes. The RF coupled to the endcaps lowers this potential difference and therefore the q_z of the ions. Once this RF was nulled, the q_z of the ions increased. This is the first known report of the effect of the RF which couples to the endcaps. Although standard mass calibration compensates for this coupled RF, any attempt to calculate the q_z of ions from measurements of the ring RF voltage must take this into account to prevent a systematic error.

These ion frequency measurements can be converted to measured q_z values. For m/z 195.1, the ion frequency was measured to be 68.065 kHz ($q_z=0.250143$) without the null circuit and 68.196 kHz ($q_z=0.250618$) with the null circuit. The RF voltage applied to the ring electrode is approximately 249.6 V_p; approximately 0.46 V_p of RF couples to the endcaps. The ratio of the ring to endcap potential difference with the null circuit to that without the null circuit is approximately

$$\frac{249.6}{249.6 - 0.46} = 1.00184 \quad (4-5)$$

This ratio can be compared to the ratios of the measured q_z with the null circuit divided by that without the null circuit, since q_z is directly proportional to the RF voltage.

$$\frac{0.250618}{0.250143} = 1.00190 \quad (4-6)$$

For m/z 1522, the ion frequency was measured to be 68.024 kHz ($q_z=0.249997$) without the null circuit and 68.152 kHz ($q_z=0.250458$) with the null circuit. The RF voltage applied to the ring electrode is approximately 1947 V_p and approximately 3.6 V_p of RF couples to the endcaps. Comparing the same ratios

$$\frac{1947}{1947 - 3.6} = 1.00184 \quad (4-7)$$

$$\frac{0.250458}{0.249997} = 1.00184 \quad (4-8)$$

These two sets of ratios are similar enough that the RF coupling to the endcaps can be assumed to be causing the shift in the q_z of the ions. By taking into account, or nulling, the RF on the endcaps, a more accurate calculation of the q_z of the ions can be made from the RF voltage applied to the ring.

AC Offset Amplifier Circuit

With the coupling of the ring RF voltage to the endcaps minimized, the next step was to add the AC offset by driving the additional transformer T4 shown in Figure 4-18. To do this, a second LCQ octopole RF generator was modified and added. It required two main inputs, a sinusoidal reference voltage at the desired frequency and a 0 to 10 V control signal which determined the output voltage of the amplifier. The AC offset frequency was generated using a direct digital synthesizer (DDS) which is a computer controlled circuit which generates sinusoidal reference voltages of various frequencies. There are three DDSs on the waveform/DDS PCB in the LCQ which produce the sinusoidal reference voltages for the main RF frequency, the resonant excitation / ejection frequency, and the octopole RF frequency (see Figure 1-6). The resonant excitation / ejection DDS was chosen to generate the reference sinusoid for the AC offset. In place of the resonant excitation / ejection DDS, the octopole RF DDS was used. An external function generator (Wavetek Model 275, San Diego, CA) was used to provide the octopole RF frequency of 2.43 MHz since this is a static frequency which does not require computer control.

The main reasons for using the DDSs to generate both the RF drive frequency and the AC offset frequency is that the output frequency must be very stable and the two sinusoids must remain in perfect phase synchronization. The DDS circuits built into the LCQ run off the same clock chip meaning that the DDSs will output exactly the same frequency if so programmed and the phase relationship between them will not drift. The DDS chips used can be programmed to start at any arbitrary phase, allowing multiple DDS channels to be programmed with a given phase difference, ϕ_{AC} . However, the LCQ software does not offer this function and the DDS channels always start at 0° . To get around this limitation and allow the phase synchronization of two DDS channels, the AC offset channel was started at a variable frequency around 1 kHz for 1 ms during the first scan table. The frequency was then changed to the RF drive frequency, 760 kHz, in the second scan table which was the real start of the scan. Since a change in frequency does not reset the phase of the output, the frequency of the first table can control the relative phase of the two 760 kHz sinusoids. This is shown graphically in Figure 4-21.

The AC offset amplitude was controlled with a 0 V to 10 V control signal from the SPARE1 DAC on the main system board. A potentiometer was used to zero the output of the AC offset generator to insure that it completely turned off when the control signal, SPARE1, was set to zero. The turns ratio, 24:10, of transformer T4 in the modified balun circuit was chosen to match the impedance of the endcap circuit to the amplifier. With this choice, the AC offset generator was capable of supplying a maximum of 18 V_p to the endcap electrodes.

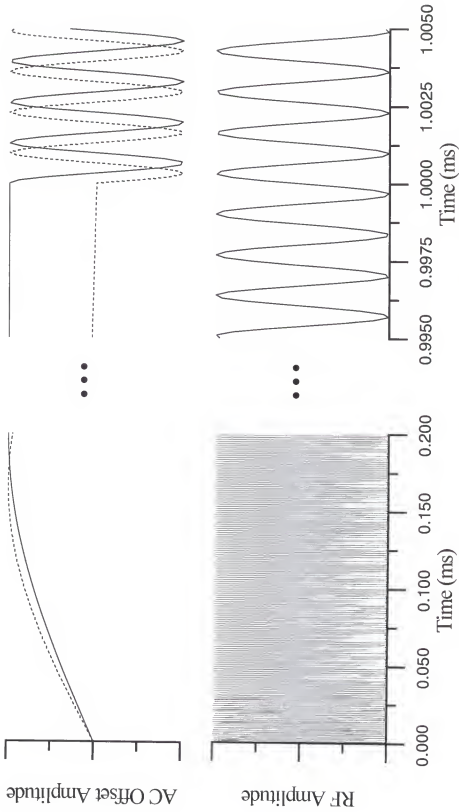


Figure 4-21 – Graphical representation of method used to control phase relationship between the RF drive frequency and the AC offset frequency. At 1.0 ms, the AC offset frequency is changed from 1.25 kHz (solid line) or 1.5 kHz (dotted line) to 760 kHz to match the RF drive frequency.

Phaser Math

Using the circuitry shown in Figure 4-18, the AC offset could be applied to the endcap electrodes. To apply the AC offset to the ring electrode as well, no additional electronics are needed if some simple phaser math is used. Including the AC offset, the voltage applied to the ring electrode is the sum of two sinusoidal voltages with the same frequency. This summation can be replaced with a single sinusoidal voltage of the same frequency and a different phase. By representing the sinusoidal voltages as phasers, this transformation can easily be seen. Phasers are simply vectors whose length is the magnitude of the voltage and whose angle is the phase angle of the voltage. In Figure 4-22, the voltages applied to the ring and endcap electrodes are shown as phasers. The phase angle between the RF voltage, V_{RF} , and the AC offset, V_{TrapAC} , is shown as ϕ_{AC} . Simple vector addition gives the resultant RF voltage phaser, V_{RF}' . From the resulting magnitude and phase angle of V_{RF}' , the equivalent single sinusoidal RF voltage to apply to the ring electrode can be calculated. The vector calculations and this new set of phasers are shown in Figure 4-23. For $0^\circ \leq \phi_{AC} \leq 180^\circ$, equation 4-9 can be used to compute the new RF voltage amplitude, V_{RF}' , and equation 4-10 can be used to compute the new phase difference between the RF voltage and the AC offset, ϕ_{AC}' .

$$V_{RF}' = \left[V_{RF}^2 + V_{AC}^2 - 2 \cdot V_{RF} \cdot V_{AC} \cdot \cos(\phi_{AC}) \right]^{\frac{1}{2}} \quad (4-9)$$

$$\phi_{AC}' = \arccos \left[\frac{V_{RF}^2 - V_{AC}^2 - V_{RF}'^2}{2 \cdot V_{AC} \cdot V_{RF}'} \right] \quad (4-10)$$

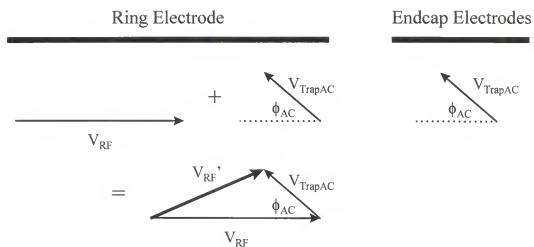
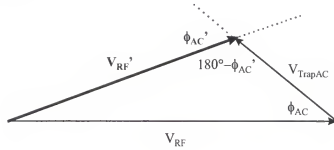


Figure 4-22 – Phasor diagram showing the voltage applied to the ring electrode as the summation of the RF trapping voltage, V_{RF} , and the AC offset, V_{TrapAC} . The voltage applied to the endcap electrodes is V_{TrapAC} .

For $0^\circ \leq \phi_{AC} \leq 180^\circ$



For $180^\circ < \phi_{AC} < 360^\circ$

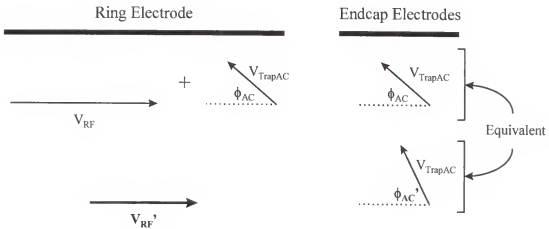
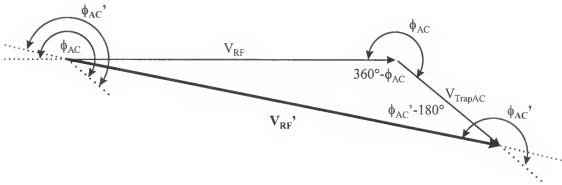


Figure 4-23 – Phaser diagram showing vector math to determine the resultant RF voltage to be applied to the ring electrode, V_{RF}' , and the new relative phase, ϕ_{AC}' .

For $180^\circ < \phi_{AC} < 360^\circ$, equation 4-11 can be used to compute the new RF voltage magnitude, V_{RF}' , and equation 4-12 can be used to compute the new phase difference between the RF voltage and the AC offset, ϕ_{AC}' .

$$V_{RF}' = \left[V_{RF}^2 + V_{AC}^2 - 2 \cdot V_{RF} \cdot V_{AC} \cdot \cos(360^\circ - \phi_{AC}) \right]^{\frac{1}{2}} \quad (4-11)$$

$$\phi_{AC}' = \arccos \left[\frac{V_{AC}^2 + V_{RF}'^2 - V_{RF}^2}{2 \cdot V_{AC} \cdot V_{RF}'} \right] + 180^\circ \quad (4-12)$$

Software was written to calculate these values automatically and adjust the RF voltage and phase relationship. The phase relationship between the RF trapping voltage and the AC offset needed to be calibrated because of the different time delays associated with the RF generator and the AC offset circuitry. The RF trapping voltage was not measured directly because the capacitance of the scope probe adversely affected the tuned RF circuit. Instead, the low voltage side of the secondary of the main RF transformer coil was measured. The RF on the ring electrode was assumed to be 180° out-of-phase with the low voltage side of the secondary because of the phase shift through an inductor coil. The instrument control software was modified to compute the necessary phase difference between the two reference sinusoids in order to get the desired phase relationship on the electrodes.

AC Offset Coupling to the Ring Electrode

When the AC offset was added to the endcaps, capacitive coupling from the endcap electrodes was seen to the ring electrode. This has the undesirable effect of altering the q_z of the ions because the amount of RF on the ring electrode is changed. This was ironic since a fair amount of effort had been placed into nulling the RF on the

ring electrode which capacitively coupled to the endcaps. Fortunately, this same circuitry which minimized coupling from the ring to the endcaps was found to also minimize the coupling from the endcaps to the ring. The original tuning of the nulling capacitors, C_{EN} and C_{EX} , used an oscilloscope connected to the endcaps to measure the amount of coupling. However, the oscilloscope could not accurately measure voltages below 5 mV_{pp}, so the best null was not obtained. By fine tuning these capacitors, both paths for coupling could be reduced even further. A very accurate measure of the amount of coupling to the ring electrode was necessary and the RF detector seemed the logical choice. The RF detector provides the feedback for a linear control system which regulates the amount of RF voltage on the ring electrode. By running the RF control system open loop, the RF generator outputs a constant voltage and the RF detector can be used to measure the amount of RF on the ring electrode. To determine the amount of RF on the ring which was coming from capacitive coupling, a special scan was set up. This scan toggled between a AC offsets of 16 V_p and 0 V_p every 2 ms while a low RF voltage was applied to the ring electrode. The amount of detected RF changed with the application of the AC offset to the endcap because of capacitive coupling. The nulling capacitors, C_{EN} and C_{EX} , were fine tuned (changed by a few pF) using air dielectric variable capacitors to minimize the change in the detected RF with the application of the AC offset. The coupling could not be eliminated but was reduced so that an AC offset of 16 V_p caused no more than a 0.5 mV_{Det} change in the detected RF. This detected RF voltage can be converted to absolute voltage on the ring using the approximate relationship

$$\frac{8900 V_p}{10 V_{Det}} \cdot 0.5 mV_{Det} = 0.4 V_p \text{ coupled to ring} \quad (4-13)$$

This corresponds to a percentage of $0.4/16=2.8\%$ of the AC offset on the endcaps which couples to the ring electrode. Although any coupling is undesirable, the amount has been reduced to a level which will not affect the q_z of ions inside the ion trap to a very large extent.

Shielding Lens

The next step was to design and build a shielding lens such as that used in the SIMION simulations (Figure 4-14b) which could fit between the octopole and the entrance endcap (Figure 4-24). The lens was designed to mimic the shape of the inside of the endcap, allowing the lens to be positioned as close as possible to the endcap. The entrance endcap was bored out (Figure 4-25) to accommodate a macor insulating ring (Figure 4-26). The lens (Figure 4-27) was then inserted into the back of the insulating ring and a standard LCQ octopole then fit into the back of the lens. Because of the extra space required between the lens and the endcap plus the thickness of the lens itself, the ion trap was moved closer to the detector by 0.070 in. No adverse effects were observed; in fact, no arcing was observed even when the ion trap was moved 0.115 in closer to the detector. The SPARE3 DAC on the system board was used to provide a DC offset, V_{LensDC} , of up to ± 130 V to the lens.

Experiments Varying Trap Offset with Shielding Lens

With the shielding lens in place, experiments were performed for different values of V_{TrapAC} and ϕ_{AC} . For all of these experiments, the DC offsets were -3 V on the first octopole and -6.5 V on the second octopole. The inter-octopole lens was held at -45 V.

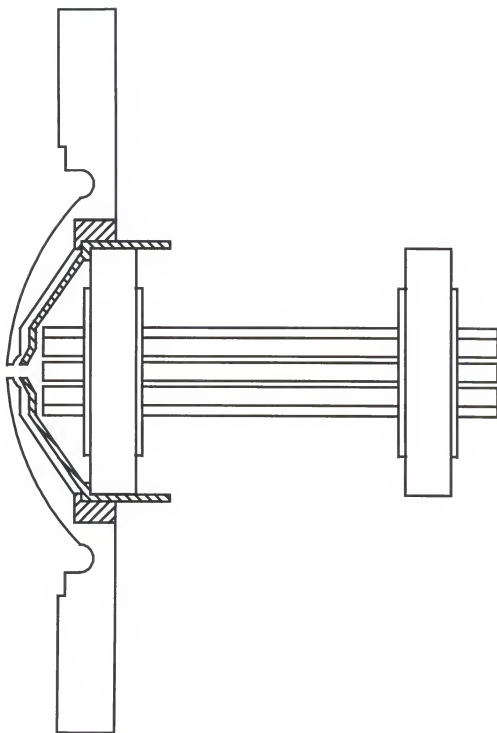


Figure 4-24 – Assembly drawing showing how octopole fits into back of lens, the lens fits into the insulating ring, and the ring fits into the back of the bored out entrance endcap.

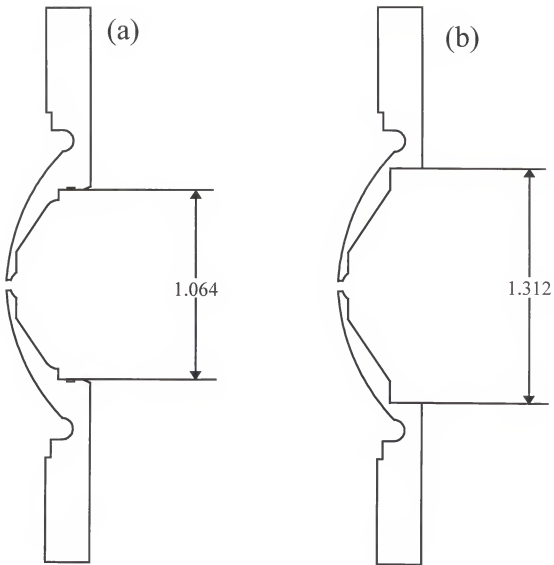


Figure 4-25 – Drawing of entrance endcap showing how (a) standard endcap was (b) bored out to accommodate insulting ring and shielding lens.

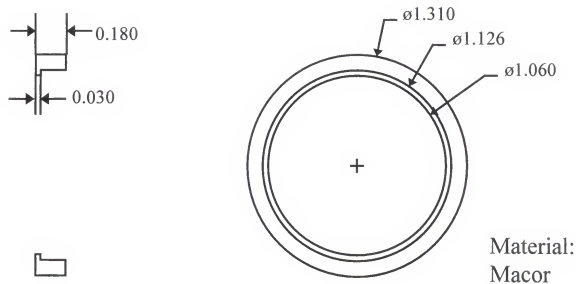


Figure 4-26 – Drawing of macor insulting ring.

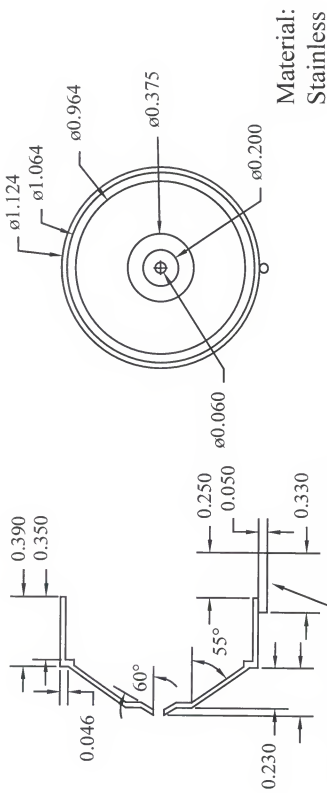


Figure 4-27 – Drawing of shielding lens placed outside entrance endcap.

For m/z 106.1, a LMCO during injection of 35 ($q_z=0.297$) was used for a V_{TrapDC} of -10 V. To determine an appropriate shielding lens voltage, V_{LensDC} was varied between -50 V and 0 V and the resulting ion signal was recorded (Figure 4-28). At voltages more negative than -6 V, the ion signal remained essentially constant, so a lens voltage of -8 V was chosen. The ion signal was then recorded under various circumstances with respect to a V_{TrapAC} of 0 V_p to measure the change in trapping efficiency caused by the AC offset. The relative ion signal is shown in Figure 4-29 for ϕ_{AC} values between 0° and 355° in increments of 5° and V_{TrapAC} values of 5 V_p, 10 V_p, and 15 V_p. For ϕ_{AC} phase differences between approximately 100° and 180°, the ion signal was higher with the AC offset than without it. For other ϕ_{AC} values, the ion signal was lower than without the AC offset. The application of the AC offset at an appropriate phase difference increased the trapping efficiency of the m/z 106.1 ions, as predicted by the computer simulations (Figure 4-15).

Effects of Experimental Parameters of Phase-Sympathetic Injection

Encouraged by the positive results from experiments using phase-sympathetic injection, a better characterization of many of the experimental parameters was performed. Since LMCO during injection is known to dramatically affect the efficiency with which injected ions are trapped, the effect of LMCO when using phase-sympathetic injection was also studied. With V_{TrapAC} set to 0 V_p, the relative ion signal was measured as a function of LMCO during injection for six different m/z ions (Figure 4-30). From these data, LMCO values were chosen to use with phase-sympathetic injection. LMCO values were chosen (shown by solid circles in Figure 4-30) on the leading edge of the optimum, at the optimum, and on the falling edge of the optimum. Because of the broad optima for m/z 106.1 and 195.1, another LMCO was chosen for these ions as well. The

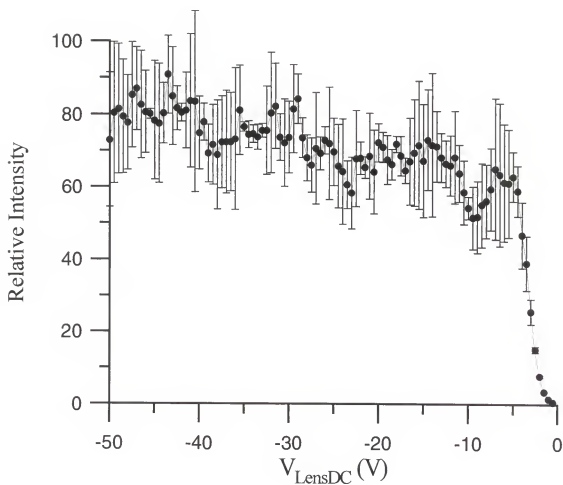


Figure 4-28 – Variation of m/z 106.1 ion signal for various DC voltages applied to shielding lens. q_z during injection=0.297; $V_{\text{TrapDC}}=-10$ V. Error bars correspond to one standard deviation for 3 replicate measurements.

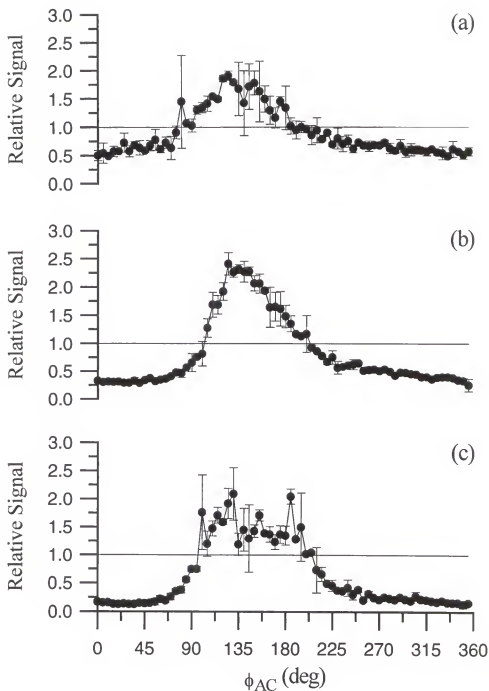


Figure 4-29 – Relative ion signal for m/z 106.1 as a function of ϕ_{AC} for V_{TrapAC} of (a) $5 V_p$, (b) $10 V_p$, and (c) $15 V_p$. Signals relative to $V_{TrapAC}=0 V_p$. Error bars correspond to one standard deviation for 3 replicate measurements.

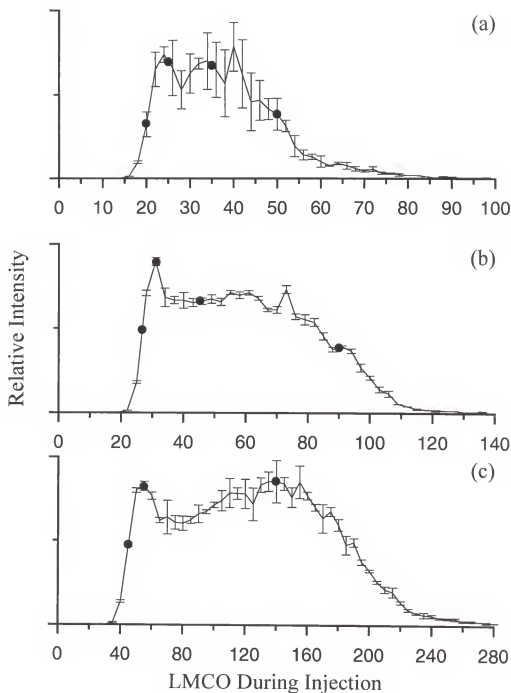


Figure 4-30 – Effect of LMCO during injection for six ions of m/z (a) 106.1, (b) 195.1, (c) 524.3, (d) 1222, (e) 1522, and (f) 1822. No AC offset voltage was applied. Error bars correspond to one standard deviation for 3 replicate measurements. The ● symbols represent the LMCO values chosen for study with phase-sympathetic injection.

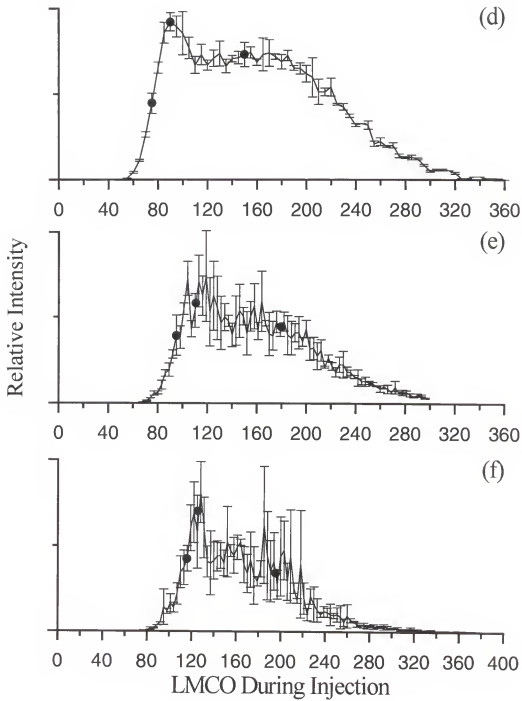


Figure 4-30 – continued.

signal for six different m/z ions was recorded at different LMCO values, V_{TrapAC} , and ϕ_{AC} . The signal was measured relative to V_{TrapAC} of $0 V_p$ at the optimum LMCO for each m/z ion as shown in Figure 4-30. The V_{TrapAC} was varied between 0 and $18 V_p$ in $3 V_p$ increments, while ϕ_{AC} was varied between 0° and 350° in 10° increments. All of these data were compiled into a series of contour plots where the relative improvement in trapping efficiency was plotted as a function of V_{TrapAC} and ϕ_{AC} . The contour plots for m/z 106.1 are shown in Figure 4-31 for four different injection LMCO values. The largest improvement in signal using phase-sympathetic injection occurred at the LMCO which was determined to be optimum without phase-sympathetic injection. This is interesting because it implies that the same LMCO that would otherwise be used with normal ion injection will produce the greatest trapping efficiency when the AC offset is applied. At this LMCO, a V_{TrapAC} of $9 V_p$ at a ϕ_{AC} of 140° produced the largest improvement in trapping efficiency, a factor of 2.5. Similar contour plots for other m/z ions are shown in Figure 4-32 (m/z 195.1), Figure 4-33 (m/z 524.3), Figure 4-34 (m/z 1222), Figure 4-35 (m/z 1522), and Figure 4-36 (m/z 1822). All of these plots involved a lot of work to generate, but were deemed necessary in order to better understand the interactions between all of the experimental variables. The maximum improvements in signal were observed for lower m/z ions. In addition, the optimum V_{TrapAC} increased as a function of m/z .

From all of these data, it was determined that the optimum improvement in signal occurred at a LMCO which was optimum even without the AC offset added. At this optimum LMCO, the optimum V_{TrapAC} and ϕ_{AC} are plotted as a function of m/z in Figure 4-37. At higher m/z , the optimum V_{TrapAC} increased until at m/z 1522 the maximum

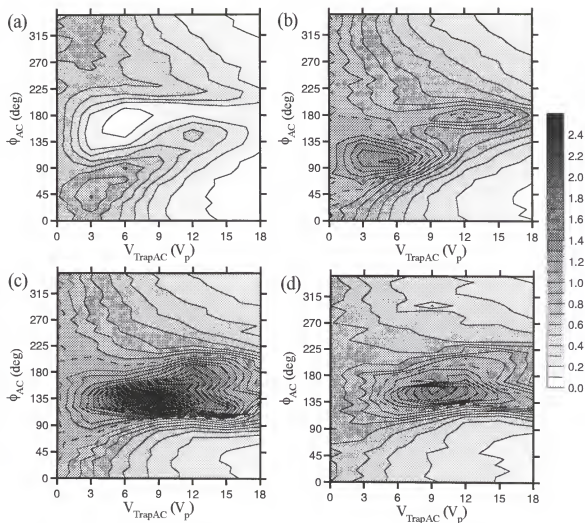


Figure 4-31 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 106.1. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0$ V_p. Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMCO=20, $q_z=0.17$, (b) LMCO=25, $q_z=0.21$, (c) LMCO=35, $q_z=0.30$, (d) LMCO=50, $q_z=0.42$.

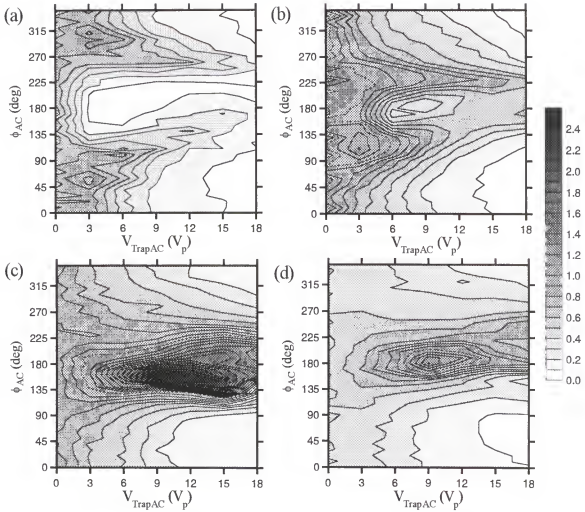


Figure 4-32 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 195.1. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0 V_p$. Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMCO=27, $q_z=0.12$, (b) LMCO=31, $q_z=0.14$, (c) LMCO=45, $q_z=0.21$, (d) LMCO=90, $q_z=0.42$.

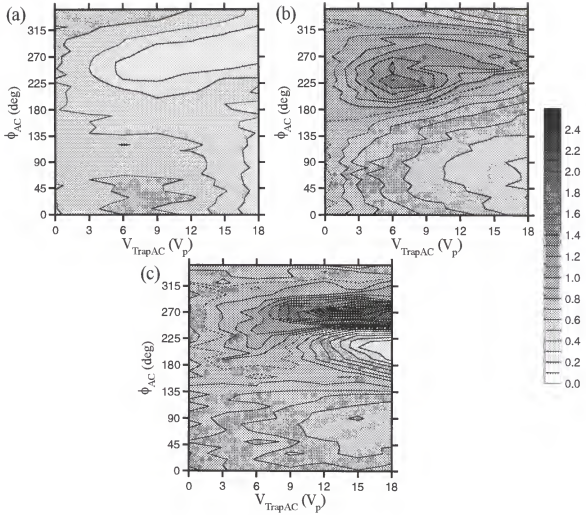


Figure 4-33 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 524.3. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0$ V_p . Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMCO=45, $q_z=0.077$, (b) LMCO=55, $q_z=0.094$, (c) LMCO=140, $q_z=0.24$.

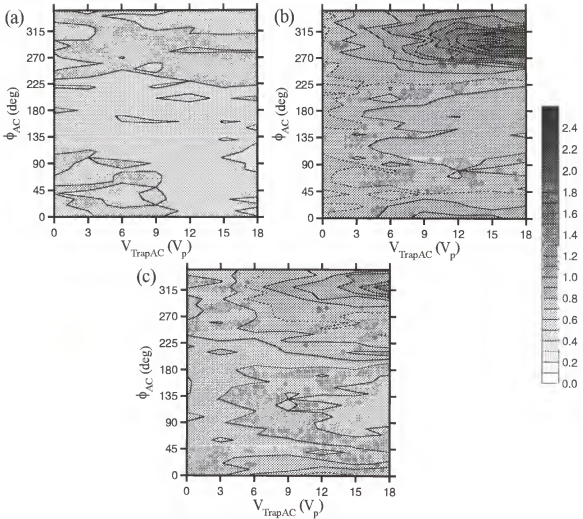


Figure 4-34 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 1222. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0 V_p$. Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMCO=75, $q_z=0.060$, (b) LMCO=90, $q_z=0.072$, (c) LMCO=150, $q_z=0.12$.

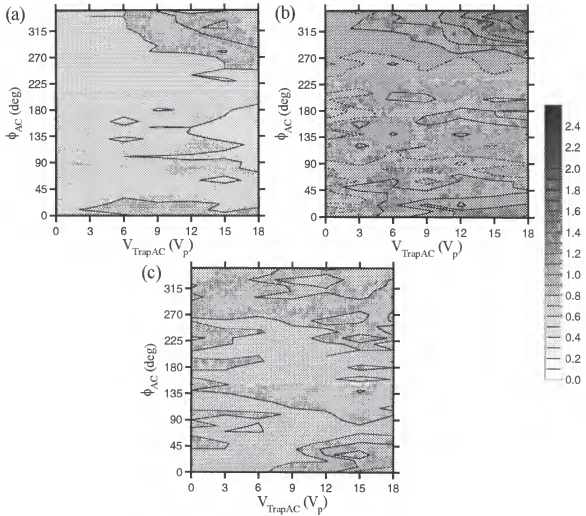


Figure 4-35 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 1522. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0 \text{ V}_p$. Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMC0=95, $q_z=0.056$, (b) LMC0=110, $q_z=0.065$, (c) LMC0=180, $q_z=0.11$.

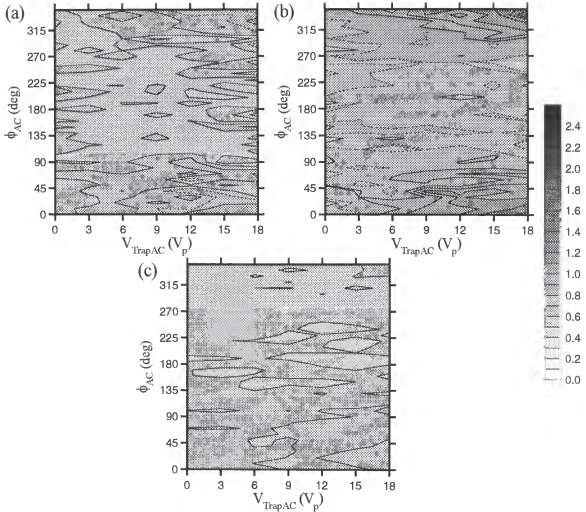


Figure 4-36 – Contour plots showing effect of V_{TrapAC} and ϕ_{AC} for m/z 1822. Detected ion signal shown relative to $V_{\text{TrapAC}} = 0 V_p$. Dotted line is shown for a relative ion signal of 1.0. Shown for (a) LMCO=115, $q_z=0.057$, (b) LMCO=125, $q_z=0.062$, (c) LMCO=195, $q_z=0.096$.

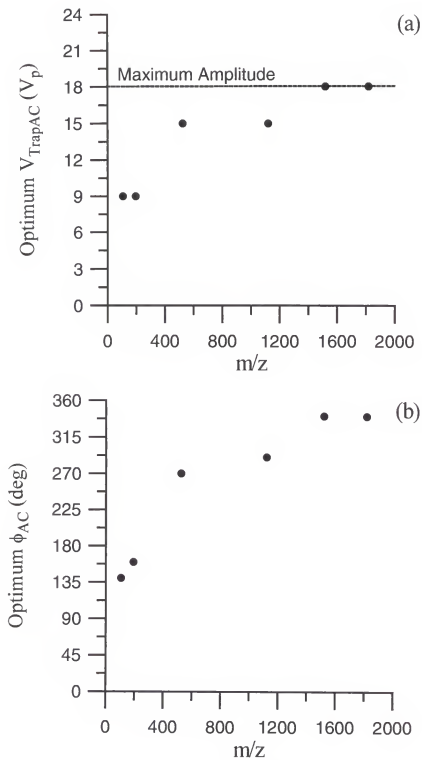


Figure 4-37 – Optimum (a) V_{TrapAC} and (b) ϕ_{AC} shown at optimum LMCO during injection.

output voltage of the AC offset amplifier was reached (18 V_p). This could be the result of increased ion momentum which requires that higher AC offset voltages be applied to the lens to affect the higher mass ions. Alternatively, a larger AC offset voltage might be necessary because the higher m/z ions are trapped at higher LMCO values and therefore the RF fringe fields are stronger. This means the AC offset voltage must be higher in order to overcome the effect of the RF fringe field.

To examine this in more detail, the optimum V_{TrapAC} was plotted as a function of m/z and LMCO (Figure 4-38). Although there is not enough data to determine a relationship, it is clear that the optimum V_{TrapAC} increases as a function of increasing m/z and LMCO. More experiments and computer simulations are needed in order to better characterize this relationship. Also, the optimum ϕ_{AC} was found to increase as a function of m/z . Again, the optimum ϕ_{AC} was plotted versus m/z and LMCO (Figure 4-39). Here, the optimum ϕ_{AC} was found to increase as a function of both m/z and LMCO; however, the relationship seems to be dominated by m/z , with the effect of LMCO secondary. It is hoped that from more such plots, it might be possible to predict the optimum experimental parameters for any arbitrary m/z . The bottom line of all this discussion is that an increase in trapping efficiency was observed for all m/z ions examined. A plot of the signal increase versus m/z is shown in Figure 4-40. Larger improvements at the higher m/z ions might be possible if larger AC offset voltages could be generated.

Other Methods of Varying Ion Kinetic Energy and Arrival RF Phase

The results from the application of an AC voltage to vary the trap offset were encouraging, but this technique is experimentally difficult to implement. It was speculated that the application of the AC offset distorted the potential field near the

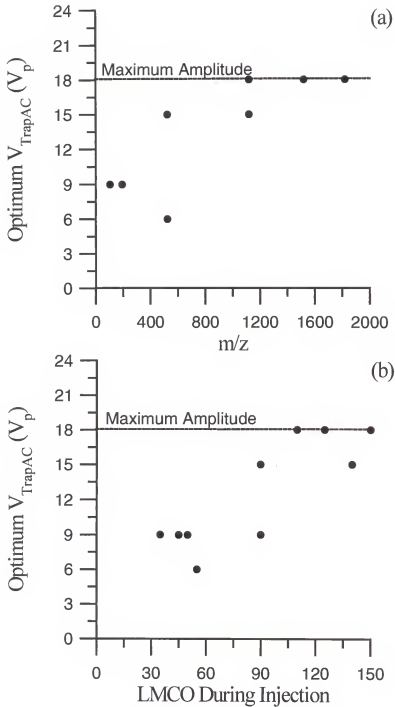


Figure 4-38 – Optimum V_{TrapAC} plotted for all LMCO during injection values as a function of (a) m/z and (b) LMCO during injection.

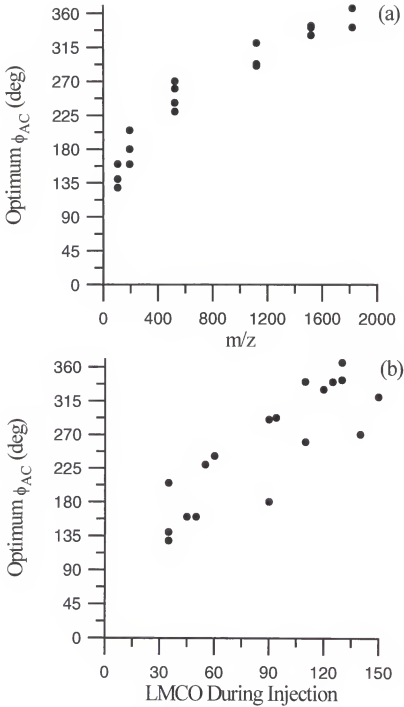


Figure 4-39 – Optimum ϕ_{AC} plotted for all LMCO during injection values as a function of (a) m/z and (b) LMCO during injection.

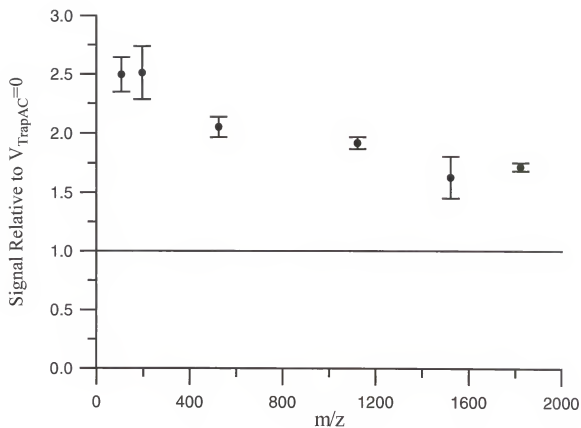


Figure 4-40 – Maximum improvement in trapping efficiency using phase-sympathetic injection and AC offset applied to trap offset. Error bars correspond to one standard deviation for 3 replicate measurements.

endcap hole so that ions were slowed down and speeded up as they approached the ion trap. The addition of the shielding lens was first thought to prevent ions from being lost due to interactions with the AC offset voltage when they were still far from the ion trap. However, the AC offset was found to produce similar improvements without the shielding lens, although to a much lower extent. In fact, with the maximum V_{TrapAC} of 18 V_p an improvement of only 1.8 was obtained compared to an increase of 2.5 with a V_{TrapAC} of only 9 V_p when the shielding lens was used. It appears that the shielding lens not only shields the ions, but it concentrates the electric field near the endcap. Instead of the field from the AC offset extending far into the octopole, placing the lens outside the endcap concentrates the AC offset field in the small distance between the endcap and the lens. This creates stronger fields on the ions and allows manipulation of the ion beam with smaller AC offset voltages. With this in mind, it might be possible to affect the ion beam by applying the AC offset voltage to the lens outside the endcap, greatly simplifying the electronics and software. In other words, if the main purpose of the lens is to concentrate the field from the AC offset applied to the trap offset, applying the AC offset to the lens should have the same effect.

Experiments Varying Offset on Shielding Lens

The hardware and software were modified to apply an AC offset, V_{LensAC} , and a DC offset, V_{LensDC} , to the lens outside the endcap, while the ion trap was held at a constant DC offset, V_{TrapDC} . For all of these experiments, the DC offsets were -3 V on the first octopole and -6.5 V on the second octopole. The inter-octopole lens was held at -45 V. For m/z 106.1, a LMCO during injection of 35 ($q_z=0.297$) was used for V_{TrapDC} of -10 V. The ion signal for V_{LensAC} of 8 V_p and V_{LensDC} of -12 V relative to V_{LensAC} of 0 V_p

is shown as a function of ϕ_{AC} in Figure 4-41. For ϕ_{AC} phase differences between approximately 285° and 25° , the ion signal was higher with the AC offset than without it. A maximum increase in efficiency of 3.3 occurred around a ϕ_{AC} of 315° . For other ϕ_{AC} values, the ion signal was lower than without the AC offset. To further study the effects of varying the lens voltage, the V_{LensDC} was varied between -32 V and -6 V in increments of -4 V, the V_{LensAC} was varied between $2 V_p$ and $12 V_p$ in increments of $2 V_p$, and ϕ_{AC} was varied between 0° and 355° in increments of 5° . The ion signal recorded was measured with respect to that with a V_{LensAC} of $0 V_p$. The relative ion signal at the optimum ϕ_{AC} is shown for various V_{LensAC} and V_{LensDC} values in Figure 4-42. The largest signal increase occurred for a V_{LensAC} around $8 V_p$. Just as when the AC offset was applied to vary the trap offset, applying the AC offset to the lens outside the endcap increased the trapping efficiency of the m/z 106.1 ions.

The question still remained whether the application of the AC offset to the lens outside the endcap was having the same effect on the kinetic energy and RF phase at which ions arrived at the ion trap. A series of simulations were run for the case of $V_{LensDC} = -8$ V, $V_{LensAC} = 6 V_p$, and $\phi_{AC} = 300^\circ$. As before, ions of m/z 100 were started outside the ion trap ($z_{init} = 19$ mm, $x_{init} = 0.2$ mm, $y_{init} = 0$ mm, and $\Theta = 0^\circ$) with $E_0 = 3.5$ eV (ions enter the ion trap with approximately 7 eV). The ion trap was held at a q_z of 0.25. To see what effect the AC offset was having on the ions, the kinetic energy and time ions arrived at the inner plane of the entrance endcap were recorded. As was the case for applying the AC offset to vary the trap offset, varying the voltage on the lens as a function of RF phase distorted the arrival time of the ions (see Figure 4-43a). In addition, the AC

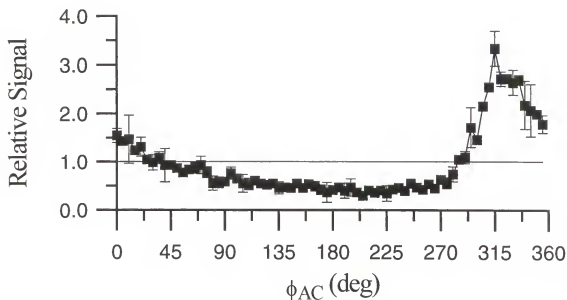


Figure 4-41 – Relative ion signal for m/z 106.1 as a function of ϕ_{AC} for AC offset applied to lens outside endcap. $V_{LensAC} = 8 V_p$. $V_{LensDC} = -12 V$. Signals relative to $V_{LensAC}=0 V_p$. Error bars correspond to one standard deviation for 3 replicate measurements.

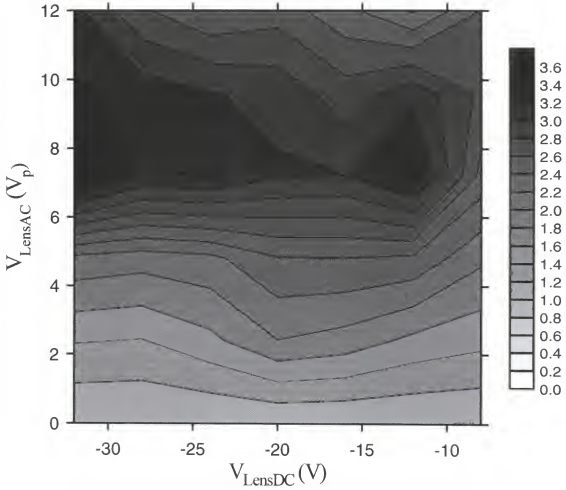


Figure 4-42 – Contour plot showing effect of AC offset and DC offset applied to lens outside endcap for m/z 106.1. The relative signal is shown for the optimum ϕ_{AC} and is relative to that obtained at $V_{\text{LensAC}} = 0 \text{ V}_p$.

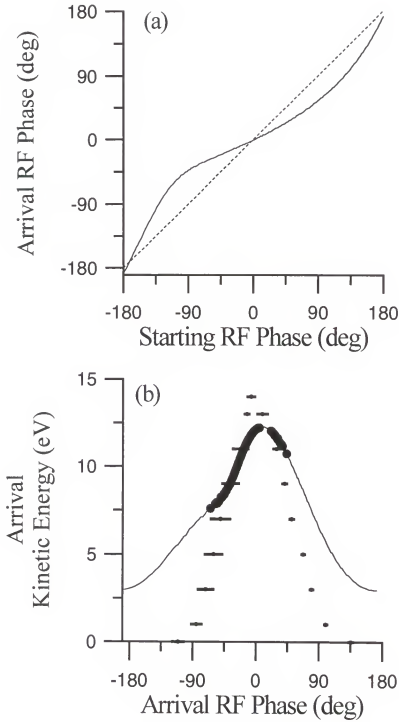


Figure 4-43 – Simulated variation of (a) the arrival RF phase versus the starting RF phase and (b) the arrival kinetic energy versus the arrival RF phase. $V_{\text{LensAC}}=6 V_p$, $\phi_{\text{AC}}=300^\circ$, and $V_{\text{LensDC}}=-12 V$. m/z 100, $q_z=0.25$, $E_0=3.5 \text{ eV}$.

offset on the lens produced an arrival kinetic energy versus arrival RF phase relationship which more closely matched the desired relationship (Figure 4-43b).

Future Prospects for Phase-Sympathetic Injection

A novel technique, phase-sympathetic injection, has been developed and demonstrated experimentally. The technique was developed from computer simulations of ion injection which suggested that ions which enter the ion trap with different kinetic energies were trapped at different RF phases. Computer simulations were used to investigate ways of manipulating a continuous beam of ions so that ions arrived at the ion trap with a kinetic energy appropriate for that RF phase. This allowed the technique to be tested and refined before time-consuming hardware and software modifications were made to evaluate the technique experimentally. Then, a combination of experiments were performed and simulations used to better understand the results. The end result was a generalized technique which uses periodic time-varying voltages applied to vary the kinetic energy and/or the RF phase that ions enter the ion trap.

The desired variation of kinetic energy and RF phase shown in Figure 4-11 suggests that improvements in trapping efficiency of 10 to 20 should be possible for m/z 100. Experimentally, only three-fold improvements have been observed for m/z 106.1. One reason, suggested by computer simulations, is the AC offset voltages used do not create an ion beam which takes full advantage of the desired kinetic energy and RF phase relationship (see Figure 4-16b and Figure 4-43b). Although the sinusoidal AC offset voltages used provided a fair amount of control over the ion beam with the DC offset, AC offset, and ϕ_{AC} , no better match with the desired relationship could be obtained. However, there is no reason why the offset voltages must be sinusoidal. In fact, non-

sinusoidal voltages would allow more control over the ion beam and may produce a kinetic energy and RF phase relationship which is more desirable. The only criterion for the voltages used is they should be periodic with the same frequency or a multiple of the RF drive frequency. The voltages must be periodic to insure that ions can be accumulated over time from the continuous ion beam. Also, other ion optics systems can be imagined which include more lenses outside the endcap to which different voltages are applied to allow even more control over the ion beam.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

By removing the restriction that ions be formed within the volume of the ion trap, it becomes possible to use a wide variety of different ionization techniques. The coupling of the ion trap with external ionization sources has allowed the high sensitivity and versatility of the ion trap to be used with practically any ion source imaginable. Although the use of external sources with quadrupole ion traps has become relatively routine, the processes by which injected ions are trapped have not been fully understood. This dissertation explored the basic concepts of trapping externally formed ions through a series of experiments and computer simulations. This type of fundamental work is needed in order to continue to develop ion trap mass spectrometry to its fullest extent.

This research was approached in a simple, straightforward manner. First, experiments were performed to study the interaction between various experimental parameters and ion injection efficiency. Second, theory and computer simulations were used to better understand the experimental observations and develop a model for ion trapping. Finally, as with any good model, the computer simulations were used to suggest new experiments; in this case to improve the trapping efficiency of injected ions.

The efficient coupling of an external ionization source to an ion trap can be broken down into two aspects: the efficient transfer of ions to the ion trap and their subsequent efficient capture and storage. Efficient transfer of ions from the ionization

source to the ion trap is accomplished using a set of ion optics to focus the ion beam. This is challenging with the electrospray ionization source studied in this work because of the high pressures involved. The large number of collisions (especially in the region just past the skimmer cone) tends to scatter the ion beam. In the Finnigan MAT LCQ, efficient transmission of ions through approximately 2 mtorr of nitrogen is accomplished using an octopole ion guide; ion losses due to scattering are minimized because the ions are contained radially by an RF field. In Chapter 2, stopping potentials were used to measure the axial kinetic energy of the ion beam. Although radial scattering losses in the first octopole were minimized, low m/z ions ($\leq m/z$ 524.3) were found to lose almost all of their axial kinetic energy through collisions. These stopping potential measurements suggested that low m/z ions may stop before reaching the inter-octopole lens. To determine whether, under standard operating conditions, ions are indeed stopped in the first octopole and therefore do not make it to the ion trap, a pressure study could be performed. By lowering the base pressure in the first octopole (by increasing the pumping speed), nitrogen could be introduced in varying amounts. Varying the pressure within the first octopole and recording the number of ions subsequently detected would give a measure of the relative efficiency of ion transmission. Stopping potential measurements could again be used to determine the amount of axial kinetic energy lost in the first octopole.

The other question raised by the experiments in Chapter 2 is the influence of the skimmer cone design on ion transmission. Of the two skimmer cones studied, the exit side of the prototype skimmer is more open compared to the commercial skimmer. The narrow tube on the exit side of the commercial skimmer more effectively prevented the

RF voltage on the octopole from affecting ions as they approached the octopole; however, there was an interesting side effect. This narrower opening in the back of the skimmer cone created a region of higher pressure, because the pumping conductance was reduced. As a result, almost all of the kinetic energy gained by ions in the supersonic expansion out of the heated capillary was lost due to collisions on the way into the octopole. Again, the large number of collisions which occur suggest that ions may be lost. A compromise between the two skimmer cone designs might be an open back design similar to the prototype skimmer that places the octopole as close as possible to the orifice. This would increase the pumping conductance out of this region (lowering the pressure) while minimizing the interaction with the RF field as ions enter the octopole.

Efficient transmission of ions is only the first step; ions must also be efficiently captured by the ion trap. The RF voltage applied to the ring electrode (measured as the LMCO or q_z) was seen to dramatically affect the trapping efficiency of injected ions. The optimum LMCO for trapping was found to vary linearly with m/z when the prototype skimmer was used. Using a simple pseudopotential well model of the trapping field inside the ion trap, a theoretical explanation for this linear variation was developed. It was based on the observation that the ion beam had a kinetic energy which increased with increasing ion mass. Extrapolating from this model, a constant kinetic energy ion beam (such as the one produced with the commercial skimmer) should result in the optimum LMCO being a function of $(m/z)^{1/2}$.

Although it was now possible to predict the optimum LMCO to trap a given m/z ion, the question still remained how to trap a range of m/z ions. Since different ions were trapped efficiently at different LMCO values, it seemed logical to step through a series of

LMCO values during ion injection. In order to choose how many injection levels and what LMCO would be used for each of those levels, a novel algorithm was developed. This algorithm used the first and last m/z of the desired scan range to calculate appropriate injection conditions.

Although the pseudopotential well model had provided a theoretical basis for the experimental trends observed, it was inadequate for quantitatively predicting the optimum LMCO. A more complex model was needed so computer simulations were used to gain more insight into ion injection. Using SIMION v6.0, ion trajectories of injected ions were calculated to determine what choices of experimental parameters resulted in successfully trapped ions. The effects of parameters such as the RF phase the ions enter the ion trap, the RF voltage applied to the ring electrode, the kinetic energy of the injected ion beam, and the pressure of helium buffer gas were studied.

SIMION was chosen because it allowed the actual electrode geometry including endcap holes to be simulated. Ion injection simulations reported in the literature always started injected ions at the endcap boundary. In addition, all of them have predicted a single, narrow range of RF phases for which injected ions are successfully trapped. However, the inclusion of endcap holes weakened the RF trapping field near the holes and allowed ions to be trapped over a second narrow range of RF phases. The endcap holes were also found to allow the RF field to penetrate out of the ion trap. SIMION provided the ability to start ions outside the ion trap (electrosprayed ions do not start at the endcap boundary) and more accurately simulate what happens experimentally. The RF field penetration was found to affect ions as they approached the ion trap. Ions were affected to a larger degree when larger RF voltages were applied to the ring or when ions

had lower velocities. Since higher m/z ions were trapped at higher RF voltages and travel at relatively slow velocities, the effect of the RF fringe field which penetrated out of the ion trap can significantly affect these ions. Ions of m/z 1522 were dramatically affected as was demonstrated by comparing simulation results when ions were started at the endcap boundary to those where ions were started outside the ion trap. Ions of m/z 1522 could be trapped at q_z values above 0.2 if started in the ion trap; however, the RF field penetration out of the endcap hole prevented these ions from ever entering the ion trap at q_z values above 0.2. This implies that simulations which start ions at the endcap boundary cannot be used to accurately model ion injection.

As a test of the accuracy of the computer simulations, the results were compared to experimental ion injection data. Simulations of the percentage of ions trapped as a function of q_z were compared to experiments. Good agreement was obtained for both m/z 100 and 1522 when a range of kinetic energy ions were simulated. This range of kinetic energies was necessary because the high pressure in the first octopole produced a statistically wide variation in the number of collisions ions experienced. The kinetic energy distribution used in the simulations was determined from the stopping potential measurements in Chapter 2.

Although the agreement between simulation and experiment was good, there were some noteworthy discrepancies. The experimental data showed much smoother variations; this was probably a result of the discrete kinetic energies which were simulated compared to an experimental ion beam which has a continuous distribution of kinetic energies. The agreement between simulation and experiment should be improved by including simulated data for even more kinetic energies. As an alternative, it might be

possible to fit an equation to the simulated data for multiple kinetic energies. If a relationship describing the variation of trapping efficiency with q_z could be determined in terms of kinetic energy, a continuous kinetic energy distribution could be described simply by integrating this relationship over all kinetic energies. This would avoid the time-consuming simulations of multiple kinetic energies.

Another possible improvement in agreement between simulation and experiment might be gained by simulating ions started at more than just a single position outside the ion trap. Ions could in fact be started over a range of initial positions and initial angles to model the randomness of a real ion beam. However, including more initial positions and kinetic energies is not practical at the current speed of the computer simulations.

It was hoped that a better understanding of the processes involved in trapping ions would lead to techniques of improving trapping efficiency. The computer simulations were used to develop a model of how injected ions are trapped. It was found that injected ions can be trapped even with the modest helium buffer gas pressures commonly used (≈ 1 mtorr) because ions naturally oscillate in the ion trap for long times (and therefore distances) at certain q_z values and initial RF phases. This allows enough collisions to occur to damp the ions' excess kinetic energy. However, the small range of favorable RF phases and the inefficiency of collisional damping demand further study to maximize the number of ions which are trapped. As a result, attention was next turned to improving the efficiency of ion trapping.

Ionization techniques such as electrospray form ions continuously and often in such low abundance that ions must be accumulated in the ion trap in order to obtain adequate signal-to-noise ratios. Although several techniques have been developed to

improve the efficiency with which injected ions are trapped, the only technique which can be used with continuous ionization sources is collisional damping. This is because all of the other techniques disturb ions which are already in the ion trap and therefore are only useful for trapping short pulses of ions. Additional methods of improving the trapping efficiency of injected ions were presented in Chapter 4.

Previous reports have shown that using higher pressures of helium buffer gas (or alternatively heavier gases such as argon) can improve trapping efficiency. However, higher pressures can adversely affect the resolution and sensitivity with which ions are detected. An alternative is to use a pulsed valve to allow a higher pressure of buffer gas to be used during ion injection; this extra buffer gas is then pumped away before mass analysis. However, the improvement in trapping efficiency may not be worth the extra time needed to pump away added buffer gas before mass analysis. This pump out time might be more effectively spent accumulating more ions under moderate and constant buffer gas pressures. With no other practical techniques available to improve the trapping efficiency from continuous ionization sources, the results of the computer simulations were revisited. From the simulations, two novel techniques of increasing trapping efficiency were developed.

The first technique was based on the observation that m/z 1522 ions were trapped with a higher efficiency than m/z 100 ions, at least in simulation. Absolute measurements of the trapping efficiency of injected ions are difficult to make experimentally; more work in this area is warranted. Even so, the simulations suggested the possibility of trapping a higher percentage of ions by using low q_z values during injection. Low q_z values can be used by simply lowering the kinetic energy with which ions are injected. It is unclear

though whether ions can be transferred efficiently to the ion trap at low kinetic energies. If not, ion losses due to scattering and defocusing may overwhelm any improvements resulting from low q_z injection.

Finally, another novel technique for improving trapping efficiency, phase-sympathetic injection, was presented. It was based on the observation that for a given m/z , ions injected at different kinetic energies were trapped at different RF phases. By applying a sinusoidal voltage at the same frequency as the RF drive voltage to vary either the trap offset or the offset on an external lens, the kinetic energy and RF phase with which ions arrive at the ion trap can be manipulated. This manipulation does not affect ions which are already in the ion trap so it can be used to accumulate ions from a continuous ionization source. In fact, three-fold experimental increases in trapping efficiency were observed for m/z 106.1. Phase-sympathetic injection is a general technique and has the potential for even larger improvements. For example, manipulating the ion beam with non-sinusoidal voltages or with new ion optic designs should allow more control over the ion beam. By creating an ion beam which more closely matches the acceptance pattern of the ion trap, an even larger percentage of ions could be trapped.

The development of phase-sympathetic injection represented a truly successful demonstration of the power of computer simulations. This work began with a series of experiments which suggested a complex relationship between trapping efficiency and several operating parameters. The processes involved in ion trapping were studied using computer simulations to provide a better understanding of the effects of the different operating parameters. Then, simulations were used to develop and test new techniques of improving trapping efficiency from continuous ionization sources. One of these

techniques, phase-sympathetic injection, was refined before time-consuming hardware and software modifications were made for experimental trials. Computer simulations such as the ones presented in this dissertation will continue to provide a better understanding of ion trap behavior. From simulations, novel methods of manipulating ions and the ion trap will certainly continue to be developed.

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BIOGRAPHICAL SKETCH

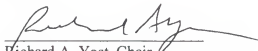
Scott Thomas Quarmby was born in Sarasota, Florida, on February 7, 1971.

Shortly after this, Scott's insatiable curiosity with the world around him became evident. At age three, during his first plane ride, Scott turned to his grandparents and asked "Will this plane come apart?". Fearing he was not coping with the experience of flying, they assured him the plane was safe and would not fall apart. This disappointed Scott because he was not scared, but instead wanted to take the plane apart. Evidently, his interest in engineering (or at least reverse engineering) began at an early age.

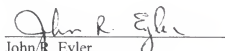
After graduation from Sarasota High School in 1988, Scott headed north to the University of Florida to study electrical engineering. It was here that Scott met his best friend and future wife Kimberly A. Machmer at the end of 1989. Although officially schooled in semiconductor design and processing, Scott became interested in mass spectrometry through a part-time job. His boss (and friend), Charles J. Schmidt, encouraged him to consider a career in analytical chemistry. Although reluctant, Scott went to talk to Richard A. Yost of the University of Florida Department of Chemistry about graduate school. Intrigued by the challenge, Scott applied and was accepted to graduate school in August of 1993. Meanwhile, he graduated with high honors in May of 1993 with a B.S. degree in electrical engineering.

In graduate school, Scott studied various aspects of quadrupole ion trap mass spectrometry from fundamentals to applications. As part of a three-year NASA Space Grant Consortium Fellowship, he spent three summers at Finnigan Corporation in San Jose, California, as an intern. Taking advantage of his multidisciplinary background, Scott worked on both electronics design and technological issues related to the fundamental operation of the ion trap. While in graduate school, Scott was awarded an Analytical Division Fellowship from the American Chemical Society and a Roger G. and Jo Bates Graduate Fellowship from the Department of Chemistry. Upon completion of his Ph.D., Scott will begin work at Finnigan Corporation in Austin, Texas, as a member of the research and engineering team.

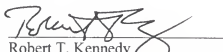
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Richard A. Yost, Chair
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


John R. Eyler
Professor of Chemistry

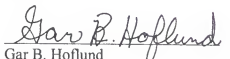
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Robert T. Kennedy
Associate Professor of Chemistry

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David H. Powell
Associate Scientist of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Gar B. Hoflund
Professor of Chemical Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August, 1997

Dean, Graduate School